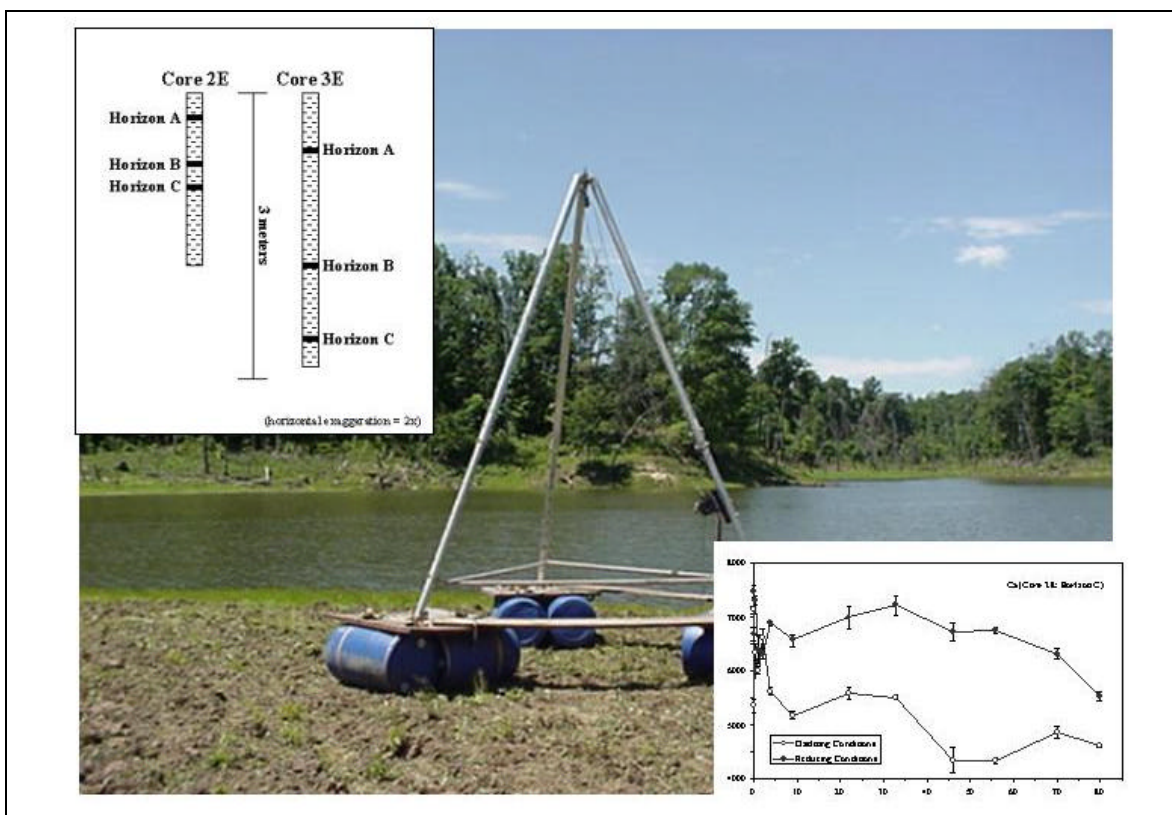


**National Sedimentation Laboratory
 Oxford, Mississippi 38655**

**Evaluation of the Potential for Trace Element Mobilization
 Resulting from Oxygenating Sediments from a Small
 Mississippi Reservoir**



**By William C. Beard III, Gregg Davidson, Sean J. Bennett, and
 Fred E. Rhoton**

CHAPTER 1

INTRODUCTION

In the 1950s and 1960s the United States Department of Agriculture-Natural Resources Conservation Service, in conjunction with local watershed project sponsors, constructed approximately 10,500 flood control reservoirs on public and private lands across the U.S. These reservoirs have provided flood control, municipal water, recreation, and wildlife habitat to the watersheds they were designed to service. They were constructed in 47 states and service a total area of more than 525,000 km², the drainage area for each being between 3 and 30 km². Their construction represents a \$14 billion national infrastructure investment. The legislation authorizing these projects includes The Flood Control Act (PL-534), The Pilot Watershed Program, The Watershed Protection and Flood Prevention Act (PL-566), and The Resource Conservation and Development (RC&D) Program (Caldwell, 2000).

Construction of these reservoirs typically involves the erection of an earthen embankment 6 to 20 meters high. The reservoir's primary spillway usually consists of a concrete or metal pipe 0.3 to 1.8 meters in diameter. This outlet pipe is placed at an elevation well above the normal lake level or "conservation pool" such that excess water that makes its way into the watershed from upstream drainage or direct rainfall can be retained and gradually released. Water flows through the emergency spillway (usually a vegetated channel) only when the water level is extremely high (Caldwell, 2000).

The average design life of these reservoirs is 50 years. More than two-thirds of them are at least 30 years old (Figure 1). As a result, the majority of them will need rehabilitation or

decommissioning over the next 20 years. Decommissioning typically results in removal of the dam. Approximately 1,800 small flood control dams will exceed their design life during the next 10 years (Caldwell, 2000).

Rehabilitation needs vary among reservoirs. A reservoir's aging manifests itself through a number of common problems. First, reservoir components like metal spillway pipes and trash guards are typically considered to have life expectancies of less than 50 years due to rust and corrosion. Second, development downstream has resulted in a greater potential for loss of life and economic damage following a dam failure, while

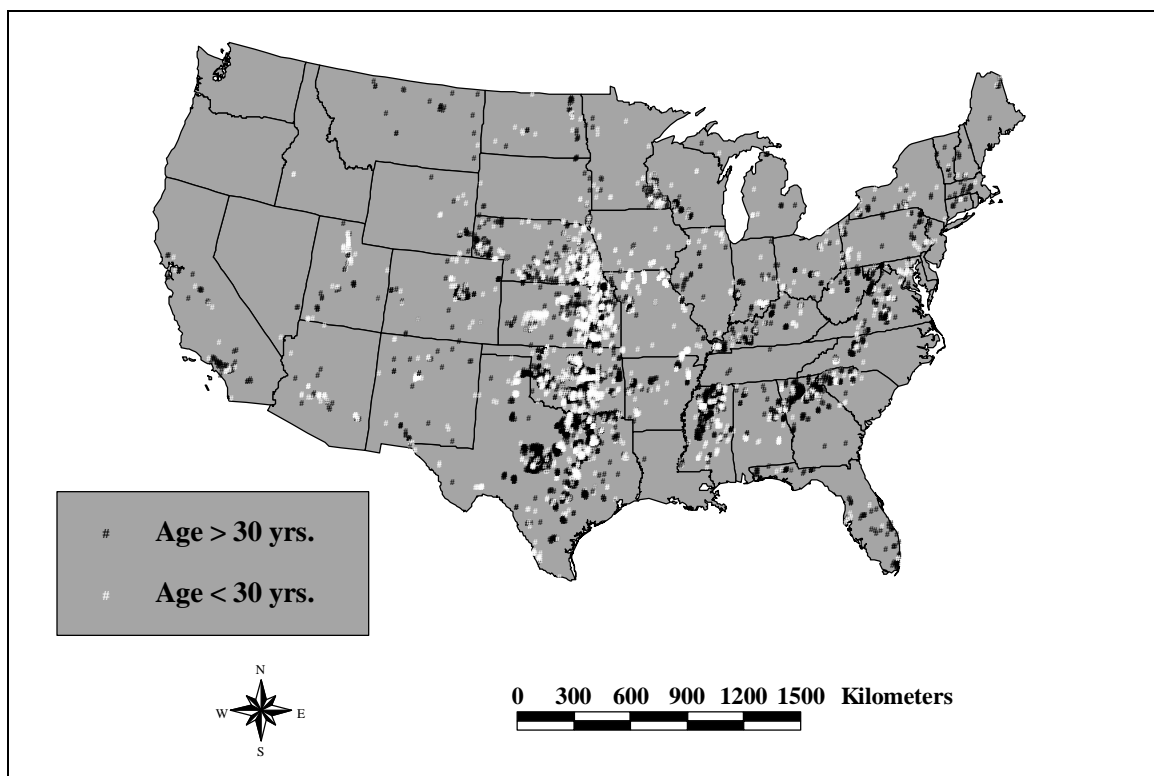


Figure 1. Location of the nation's small flood-control reservoirs constructed under the PL-534, PL-566, Pilot, and RC&D programs (U.S. Army Corps of Engineers, 2000).
upstream development like construction of parking lots and streets is contributing to the generation of runoff volumes that exceed original design plans. Third, many dams do not meet current safety regulations because safety requirements have increased in scope since their

construction. Finally, sedimentation is resulting in diminished holding capacity. This is projected to cause an increase in the frequency of flows through the emergency spillway which can increase the potential for dam breach (Caldwell, 2000).

Common approaches to the rehabilitation of these structures include dredging the reservoir and/or augmenting the dam. Each site is unique and the rehabilitation approach depends on the specific economic, environmental, and social circumstances present (Caldwell, 2000). Generally, rehabilitation is desired by landowners over decommissioning. In instances where dredging is employed, the geochemistry of the reservoir sediment is an important issue to consider because trace elements, agricultural chemicals, and other potentially toxic substances that enter waterways from runoff sources can accumulate and become concentrated in these sediments (Gambrell et al., 1976). Many contaminants have an affinity to solid surfaces like sediment particles, resulting in partitioning of aqueous contaminants to the sediment. This process, adsorption, is influenced by chemical parameters like pH and oxidation-reduction potential (Stumm and Morgan, 1970).

A study was conducted by United States Department of Agriculture (USDA) researchers at the National Sedimentation Laboratory (NSL) to physically and chemically characterize sediment from a local reservoir. Hubbard-Murphree Reservoir, constructed in the early 1960s near Charleston, Mississippi, was selected for the NSL study. The primary goal of the study was to determine the concentrations of trace elements, chemicals, compounds, and nutrients in the reservoir sediment and assess how the land-use changes over the last 40 years have affected the functionality of the reservoir. The project involved the collection and analysis of six sediment cores from the lake. Various analyses including bulk chemistry and grain size were performed on cores taken from the lake (Bennett, 2001).

The work presented herein focuses on a project supplementary to the NSL study. It was undertaken to determine the potential for the mobilization of trace elements in the reservoir sediments at Hubbard-Murphree following oxygenation due to atmospheric exposure via dredging or dam breach. The objectives were to assess the in situ geochemical conditions of the reservoir sediments at a study site and determine what effects oxygenation will have on the mobility of selected trace elements present. Reservoir sediments, like most saturated sediments, are generally anaerobic because of the low diffusion rate of oxygen through water and the speed with which oxygen is consumed during decomposition reactions (Gambrell et al., 1991a).

1.1 Description of Field Site

Hubbard-Murphree Reservoir is one of three reservoirs constructed by the Natural Resources Conservation Service (NRCS) in the Hubbard and Murphree Creeks Watershed in 1963. The lake is located approximately 4 km south of Charleston, in Tallahatchie County, Mississippi (Figure 2). Designed as medium hazard dams, a designation that refers to the potential for loss of life and property following a failure, these structures now pose a much greater public threat due to their age and an increase in local development (USDA, 2001).

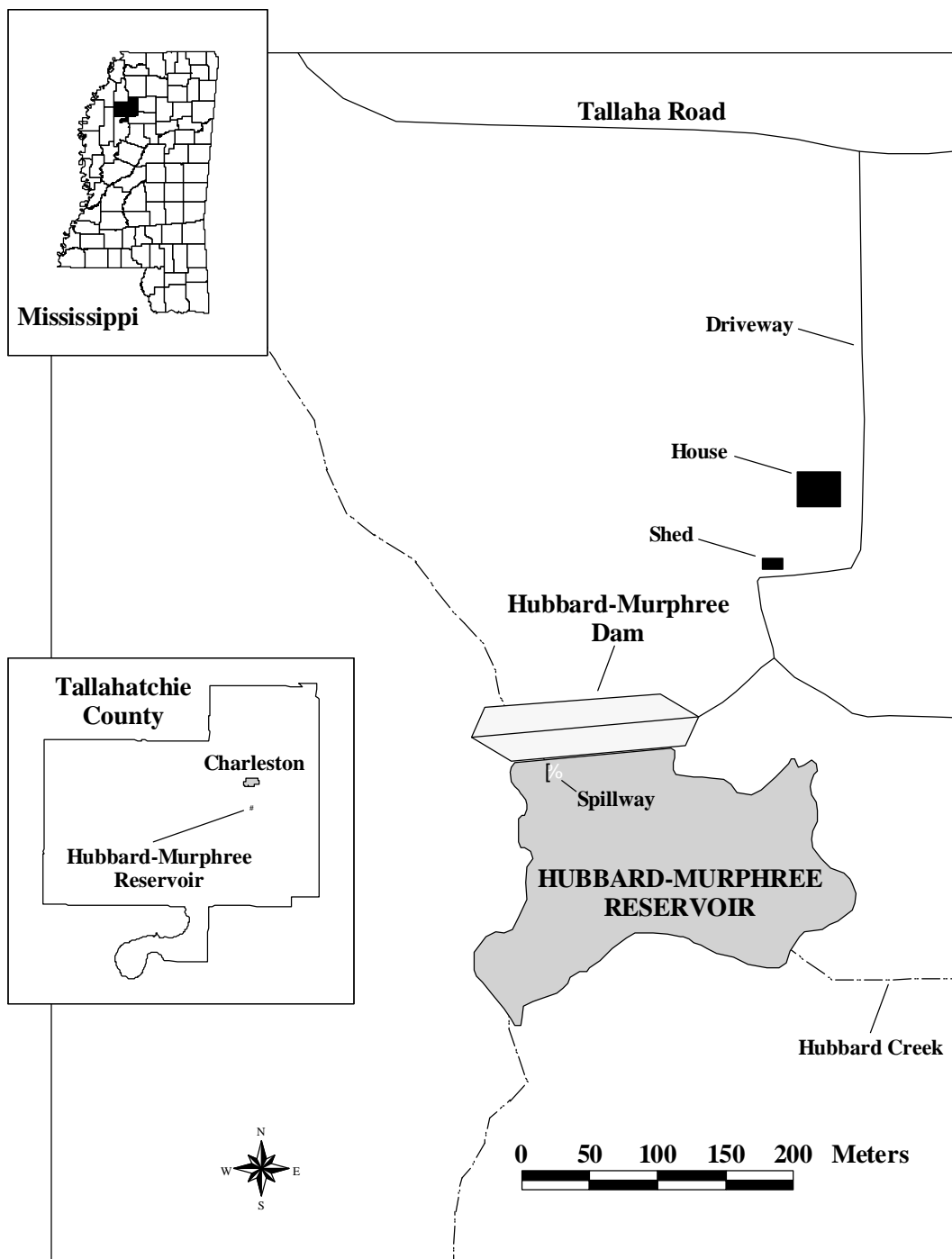


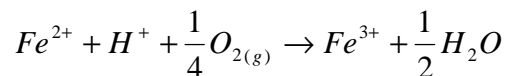
Figure 2. Location of Hubbard-Murphree Reservoir, Tallahatchie County, MS.

Hubbard-Murphree, along with the two other dams, has been selected to be part of a national pilot rehabilitation program. It is to be upgraded to high-hazard status following a number of key improvements (i.e. it will have a greater capacity so the potential for loss of life or property following a breach will be greater). These improvements include increasing the embankment and spillway riser heights to increase storage capacity. Also, the auxiliary spillway will be enlarged and lined with a geo-synthetic material to add greater capacity and stability during large storm events (USDA, 2001).

Hubbard-Murphree Reservoir has a muddy bottom and water depths of up to 2 m. It is fed primarily by Hubbard Creek. The water level is prevented from increasing due to a hole in the primary spillway pipe that is scheduled for repair during rehabilitation. A smaller unnamed creek also drains into the lake. The designed maximum sediment storage capacity for the reservoir is approximately 28,000 m³. The designed maximum floodwater storage capacity is approximately 900,000 m³. Its upstream drainage area is just over 8 km²: steep woodland, 42%; woodland, 36%; pasture, 18%; cultivated, 4% (Bennett, 2001).

1.2 Redox Chemistry Background

Oxidation/reduction (redox) reactions involve the transfer of electrons from one chemical species to another. Contrary to the principles of acid/base reactions, where free protons can exist in solution and govern pH, free electrons do not exist in solution. Redox reactions are written as a pair of half reactions such that whenever an electron is given up by one species there must be another species available to receive it (Drever, 1997). A species receiving electrons becomes reduced, while a species yielding electrons becomes oxidized. For example:



The oxidation of iron results in the reduction of oxygen. During the oxidation process the oxidizer itself is reduced.

Because oxygen so readily receives electrons from other species the process itself is called oxidation. The term oxidation originally referred to a reaction in which some element combined with oxygen (Patrick et al., 1996). However, oxygen is not the only possible oxidizer in a groundwater system. For example, NO_3^- and SO_4^{2-} can also act as oxidizers (Drever, 1997). If a system uses up all of the available oxygen and other oxidizers, then it is said to have become a strongly reducing environment. This is commonly the case when dealing with reservoir sediments where oxygen is rapidly consumed by the decomposition of organic compounds (Gambrell et al., 1991a).

Assessing the in situ redox conditions of a natural system like saturated reservoir sediments involves making oxidation/reduction (redox) potential measurements. The redox potential of a solution is a measure of the affinity of that solution for electrons. However, the redox potential of a solution cannot be measured directly, only relative to another solution. Reference electrodes are used in making redox potential measurements. The solutions they are filled with serve as references to which the solution being measured is compared. These reference electrodes are used in conjunction with a platinum-tipped metal electrode. These two electrodes used together create a completed circuit when placed in a solution to be measured (pore water for the purposes of this study). Platinum-tipped electrodes are used because platinum is an inert metal (i.e. platinum catalyzes reactions without being altered in the reaction) (Patrick et al., 1996).

The unit of measurement for redox potential is the volt. A measurement is made by connecting a reference electrode and platinum electrode to the two leads of a voltmeter (Faulkner et al., 1989). The voltage is produced by the difference in electric potential between the two cells (pore water and reference solution in this study). The voltage is reported relative to the reference solution used.

By convention, the standard reference electrode by which redox potential measurements are made is the Standard Hydrogen Electrode (SHE). The SHE is a fundamental analytical standard in electrochemistry. By convention, all half-reactions are compared to the half-reaction of the simplest element, hydrogen. This half-reaction is the oxidation of hydrogen gas (H_2) into hydrogen ions (H^+) (Figure 3). Values reported relative to the SHE are defined as Eh values. Eh simply refers to the electric potential (E°) of a solution relative to the SHE. Eh can be positive or negative depending on whether or not the activity of electrons in the solution being measured is less or greater than the activity of electrons in the SHE. Oxygenated environments typically have high Eh values (e.g. 300 to 700 mV). Reduced environments typically have low Eh values (e.g. -250 to -500 mV) (Patrick et al., 1996).

The SHE is not very practical for most applications, especially fieldwork. For this reason, other reference electrodes are generally used. A calibration factor is added to the readings made with these electrodes in order to determine Eh (Wilde et al., 1998). A typical analytical reference electrode contains a redox-sensitive element like silver or

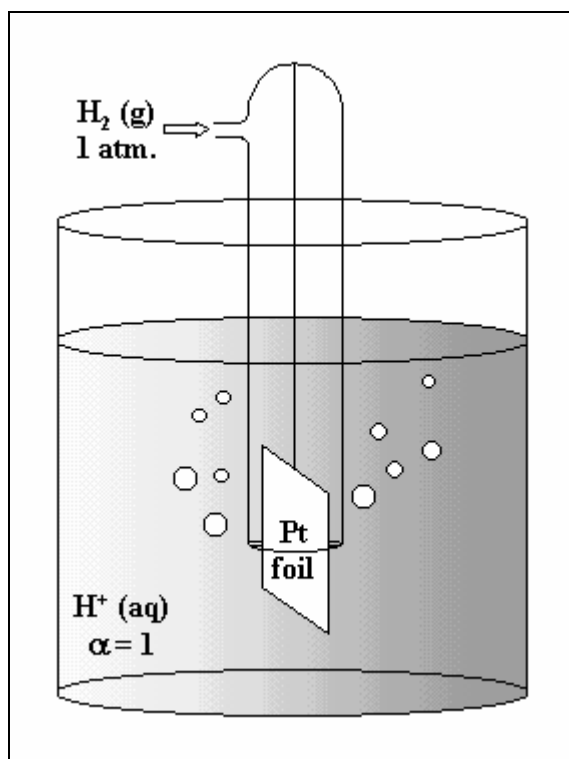


Figure 3. Illustration of the SHE. It consists of hydrogen gas being bubbled through a strong acid. Platinum foil provides a surface on which a redox reaction can take place. By definition the electric potential generated is 0.0 V (a = activity).

mercury and an electrolytic filling solution. The calibration factor added to the measurements made using the reference electrode is a function of the type of metal used in the electrode, as well as the temperature, type, and ionic strength of the filling solution used.

The redox potential of a solution is also a function of pH. Where samples have widely varying pH values, it is sometimes useful to normalize the measured Eh values to a common pH.

The relationship can be expressed by a simplified version of the Nernst equation:

$$Eh = E^{\circ} - \frac{59}{n} \log \frac{(Rd)}{(Ox)} + 59 \frac{m}{n} pH \text{ (Patrick et al., 1996)}$$

where:

E° is the standard half-cell potential

n is the number of electrons exchanged in the half-cell reaction

m is the number of protons exchanged in the half-cell reaction
 Rd is the activity of the reduced component
 Ox is the activity of the oxidized component

This equation shows that Eh increases with increasing activity of the oxidized component, decreases with increasing activity of the reduced component, and increases with an increase in hydrogen ion (H^+) activity (decrease in pH). The Eh/pH slope varies depending on the oxidants and reductants involved. Normalization of measured Eh values to a common pH of 7 is accomplished by subtracting 59 mV from the Eh measurement per pH unit for values under pH 7 and adding 59 mV to the Eh measurement per pH unit for values above pH 7. This is useful when there is a need to compare the Eh of samples independently of their pH. A normalized Eh can be calculated for use in comparisons at a common pH.

Redox potential measurements are the most accurate in anaerobic soil or water systems. High concentrations of oxygen or other oxidizers reduce the effectiveness of redox measurements because of the lack of redox active components present following oxidation. Dissolved ions facilitate the flow of electric current also improving the accuracy of the measured voltage (Faulkner et al., 1989). However, field measurements of redox potential are semi-quantitative at best. Poor reproducibility of readings coupled with the fact that most natural systems are not at chemical equilibrium make obtaining accurate readings problematic. Electrode maintenance is a must as well-maintained clean electrodes can improve measurement equilibration time and yield more accurate results. Redox potential measurements do provide an evaluation of the general intensity of oxidation or reduction and the overall redox potential of a given system, even though all of the dissolved species may not be in equilibrium at the measured Eh (Patrick et al., 1996).

Gambrell et al. (1991a) suggests that though redox measurements made with platinum electrodes are useful in determining reduction and oxidation intensity in soils, these measurements are considerably more valuable in anaerobic systems because many important chemical processes are controlled by the intensity of reduction in the system. Redox conditions of oxidized soils can be better characterized by dissolved oxygen measurements (Patrick et al., 1996).

1.3 Previous Work

Previous research on reservoir sediment chemistry is plentiful, most of it driven by the search for remediation alternatives. The effects of atmospheric exposure on dredged sediments occupy just one niche of sediment quality research. Along with trace element mobility research, studies have been conducted on the effects of dredging and oxygenation on natural and synthetic organics, as well as the speciation of individual chemical species into different forms.

Howler (1972) described how cellular respiration and chemical processes act as oxygen sinks in saturated soils. Soils that are well drained have air-filled pore spaces. Thus, oxygen is transported within them by gaseous diffusion. Saturation for extended periods of time usually results in changes in the chemical properties and microbial characteristics of soils (i.e. saturated environments usually become reducing) (Gambrell et al., 1991a).

Most methodologies for determining the potential for mobilization of trace elements involve leaching experiments that simulate reducing (in situ) conditions, oxidizing conditions, or a combination of both. Some have allowed Eh to vary during the experiment (Gambrell et al., 1991b), while others have maintained a constant Eh (Patrick et al., 1973). Patrick et al. (1973) developed a system for controlling the redox potential and pH of a sediment suspension. It was

comprised of a standard pH meter, solenoids, a reference half-cell, and meter relays. The recorder output on the pH meter was used to monitor the potential in the cell. The meter relays activated an oxygen supply system whenever the redox potential dropped to a predetermined limit. Consequently, the redox potential was prevented from dropping below that limit.

Gambrell et al. (1991b) studied the effects of a range of pH, redox potential, and salinity conditions on the release of trace elements to the soluble phase in a brackish marsh. In their leaching study they conducted 8-day incubations under varying atmospheric, Eh, pH, and salinity conditions. Their data suggested that following exposure due to dredging, the sediment would become acidified and probably release large amounts of cadmium, zinc, and nickel. This study demonstrated that solubility can be increased for some elements following dredging due to acidification even though oxidation results in a decrease in solubility for other elements like Fe.

A leaching study by Delaune and Smith (1985) compared chemical changes of freshwater sediment and saline sediment under different oxidation/reduction conditions. They concluded that the oxidation of saline sediment produced a significant drop in pH and subsequent increase in the mobility of Fe, Mn, Al, Se, Pb, Cu, Ni, Cr, Cd, and Sb. The pH dropped from neutrality to pH 3 in the saline sediments as oxidation took place. Conversely, the minimum pH produced in the freshwater sediments was 5.1. An obvious concentration difference for the same elements was not observed between the oxidizing and reducing incubations of freshwater sediment. In this case pH was the determining factor in solubility and was more pronounced in saline sediments. The presence of sulfur in the saline sediments resulted in an oxidation of sulfide to sulfuric acid following sediment aeration, thus lowering the pH significantly. This phenomenon was also observed by Pons et al. (1982), Goldhaber and Kaplan (1974), and Nordstrom (1982).

The lack of sulfur in Delaune's freshwater sediments resulted in minimal acidification following aeration.

Khalid et al. (1978) studied the effects of dissolved oxygen on the chemical transformations of several species including iron, manganese, and zinc. Reduced estuarine sediment suspensions were purged constantly with gas mixtures containing 0.11%, 2.1%, and 21% oxygen. Aqueous samples were collected at selected time intervals and analyzed for different chemical species. Increasing oxygen concentration resulted in higher redox potential and lower pH. These changes strongly affected the distribution of aqueous-phase trace elements like Fe, Mn, Cd, Cr, Zn, and As.

Myers et al. (1991) used flow-through leaching columns in a non-equilibrium experiment on contaminant mobility. Water entered through the top of a sediment column, passed through the sediment, and was chemically analyzed after exiting the system. Myers objective was to determine how long it takes for all available contaminants to be leached from a sediment body by analyzing water after it had flowed through the sediment in a column. Experiments were run continuously for a year or more. The low hydraulic conductivity of the dredged material resulted in the production of insufficient leachate volumes with highly variable chemical compositions.

Significant attention has also been paid to the chemical constituents in reservoir tailwaters, the area downstream from a reservoir dam. According to Ashby et al. (1997) the construction of a dam and reservoir changes the river downstream of the dam. In addition to alterations in the magnitude, duration, and timing of discharge, there are chemical and biological changes that result from reduced rates of oxidation both downstream from the impoundment and within the impoundment. The trends observed in the reservoir tailwaters included decreasing dissolved oxygen with depth, decreasing Eh with depth, and increasing conductivity with depth.

In the tailwaters examined by Ashby et al. (1997), elemental concentrations decreased away from the dam during high velocity flow from the spillway ($2.8 \text{ m}^3/\text{s}$) and remained relatively constant during low velocity flow from the spillway ($0.6 \text{ m}^3/\text{s}$).

According to Bennett (2001) grain size is a controlling factor on the sediment chemistry of Hubbard-Murphree Reservoir. Any variance in elemental concentrations, with depth and location, can be likely attributed to corresponding variations in the amount of clay present in a given sampling interval. The adsorption properties of clays play a significant role in the availability of various trace elements in the system.

CHAPTER 2

METHODS

2.1 Sediment Core Collection

A total of 26 sediment cores were collected from Hubbard-Murphree Reservoir during three trips from September, 2000 through August, 2001 (Figure 4). They ranged in length from 0.85 to 2.7 meters and their coordinates were recorded with a GPS receiver (Table 1). The first six cores were collected by the National Sedimentation Lab for their study (Bennett, 2001). The remaining 20 cores were collected specifically for the study presented herein.

Of the 20 cores collected for this study, most were obtained from locations in close proximity to the NSL coring locations. The result was six coring areas. This allowed for better comparison with data from Bennett (2001). Multiple cores were collected at each site to allow for multiple analyses at the same depth and location. For example, bulk chemistry analyses on two cores used in this study were compared to the grain size analyses of two cores taken from approximately the same locations.

Data used in the determination of the in situ redox potential of the sediment in Hubbard-Murphree Reservoir were collected during May and August, 2001. Twelve cores were collected during the May, 2001 trip (cores 1-6, A & B). Of these, cores 1A – 6A were used for manual on-site redox potential measurements with a voltmeter. Cores 1B – 6B were refrigerated for later bulk chemistry and leaching analyses. They were later compromised due to refrigeration failure.

The purpose of the August, 2001 coring trip was threefold. More cores were collected for in situ redox measurements with a data logger and for later bulk chemistry and leaching

analyses (cores 1C, 2C – 2E, 3C - 3E, and 4C). Of these, cores 1C – 4C were used for redox potential data logging. Cores 2D and 3D were processed for bulk chemistry analysis. Cores 2E and 3E were used in leaching experiments. Also, a nest of piezometers was installed at the site.

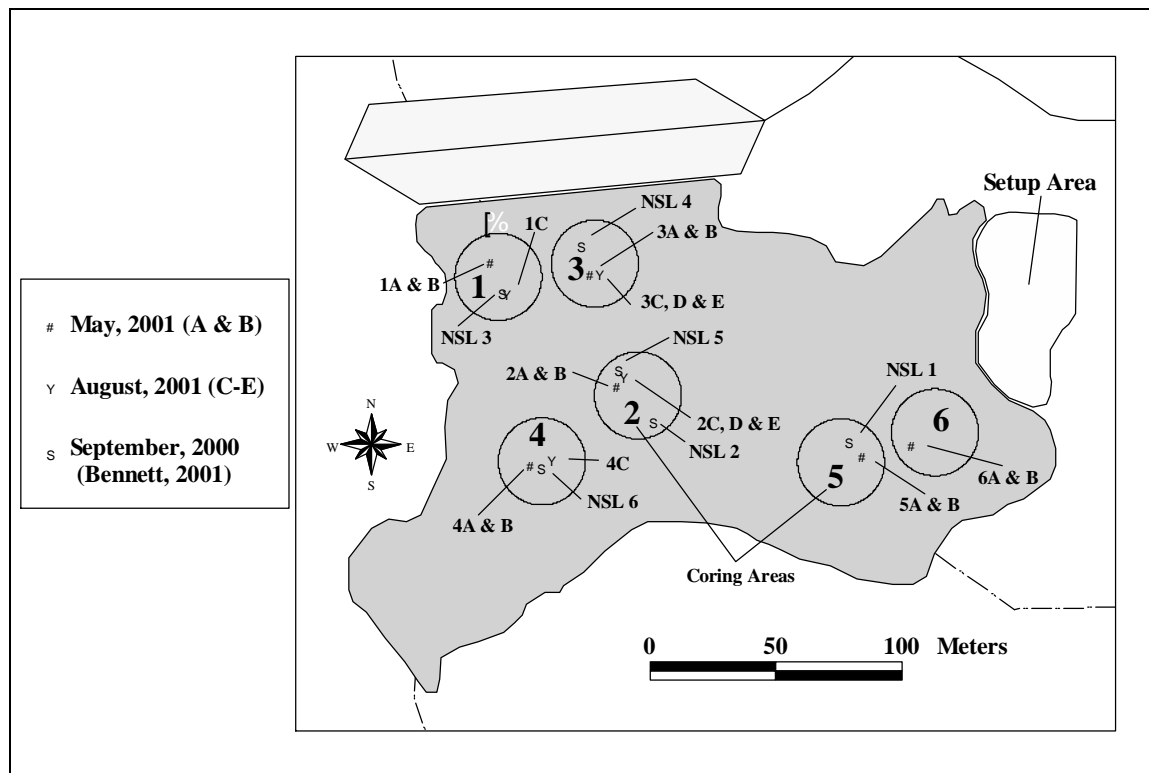


Figure 4. Coring locations at Hubbard-Murphree Reservoir. The cores obtained for this study were collected in May and August, 2001. They were collected in close proximity to the NSL's locations of cores collected in September, 2000 (Bennett, 2001).

Table 1. Length and geographic coordinates of cores collected at Hubbard-Murphree Reservoir.

Core ID	Length (m)	Latitude	Longitude
1A	1.20	N33°58'1.5814"	W90°3'15.3037"
1B			
1C	1.32	N33°58'1.1774"	W90°3'15.0477"
2A	1.70	N33°58'0.0005"	W90°3'13.3398"
2B			
2C	1.51	N33°58'0.1166"	W90°3'13.2328"
2D	1.20		
2E	1.52		
3A	1.90	N33°58'1.4384"	W90°3'13.7536"
3B			
3C	2.49	N33°58'1.4463"	W90°3'13.6105"
3D	2.54		
3E	2.40		
4A	0.85	N33°57'58.9842"	W90°3'14.6825"
4B			
4C	0.88	N33°57'59.0490"	W90°3'14.3456
5A	1.90	N33°57'59.1203"	W90°3'9.5449"
5B			
6A	2.70	N33°57'59.2525"	W90°3'8.7738"
6B			
NSL-1	1.72	N33°57'59.2884"	W90°3'9.7431"
NSL-2	1.45	N33°57'59.5370"	W90°3'12.7758"
NSL-3	1.55	N33°58'1.2014"	W90°3'15.1235
NSL-4	1.85	N33°58'1.8045"	W90°3'13.9103"
NSL-5	1.47	N33°58'0.1949"	W90°3'13.3178"
NSL-6	0.87	N33°57'58.9470"	W90°3'14.4000"

The cores were collected with a vibra-coring rig. This commercially available system consists of a vibrating 1.0 HP electric motor suspended from a winch and pulley system on a 4.2-m high floating aluminum tripod (Figure 5). Aluminum irrigation pipe with a diameter of 7.62 cm was used as core tubing. It was attached to the underside of the vibrating motor and driven into the sediment. Weights were added to the outside of the motor to facilitate the coring process. The entire rig was set up on land and pulled into the water with a small aluminum boat. The boat was also used to pull the rig to each coring location. The rig was kept stationary over the coring location by three anchors.



Figure 5. Tripod used to collect sediment cores. The rig was assembled on land and dragged into the water with a boat.

2.2 Redox Potential Measurements

The redox electrodes used in this study were fabricated using the method described by Faulkner et al. (1989). Platinum wire was cut into 1.3-cm lengths and welded to 20-cm lengths of insulated copper wire. The insulation was then slid down near the copper/platinum junction and the junction itself coated with epoxy to prevent reactions between the copper and sediment from taking place.

A commercial calomel reference electrode was used in conjunction with the fabricated redox electrodes to make redox potential measurements. Measurements were initially made with a voltmeter and later made with a multi-channel data logger which allowed for the automated recording of redox potential measurements over time. Redox potential measurements on the cores were made within a few hours of collection either on-site or in the lab. This allowed for the quantification of the in situ redox conditions of the lake sediment.

The redox potential measurements were made on cores from each of the six areas in Figure 4 (Cores 1A – 6A and 1C – 4C). The probes were inserted into the cores at 10-cm

intervals and a reference electrode was inserted in the middle of each core. The system was then allowed to equilibrate. When manual measurements were made a voltmeter's positive lead was connected to a redox probe and the negative lead was connected to the reference electrode. Measurements were taken at varying time intervals. When data logging was employed the system was set up to record the voltage at five or ten minute intervals for a specified period of time.

2.3 Piezometer Installation and Measurements

Preliminary redox potential measurements of some sediment cores suggested a trend of increasing Eh with depth. To explain this phenomenon it was theorized that there could be upwelling groundwater beneath the reservoir. Groundwater flowing under the lake from off-site would likely be more oxygenated than the pore water of the less transmissive finer-grained lake-bottom sediments. This is partly because the oxygen demand in the sandy sediments beneath the lake is likely less than the demand in the lake bottom sediments due to a higher organic content. To test this hypothesis, a nest of three piezometers was installed at the study site (Figure 6). The piezometers were installed at depths of 0.91, 1.52, and 2.13 meters below the sediment/water interface. The bottom 15.2 cm of the piezometers were screened. The insides of the piezometers were lined with plastic tubing.

The water level in each piezometer was recorded during a follow-up trip to the study site in November, 2001. Water was pumped from each piezometer using a

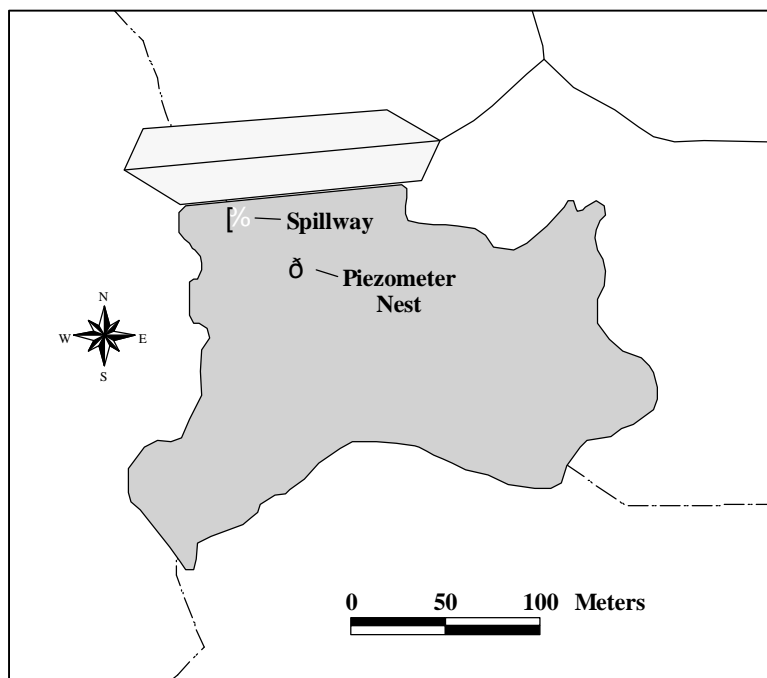


Figure 6. Location of the piezometer nest installed at Hubbard-Murphree Reservoir.

peristaltic pump and collected for chemical analysis. A water sample was collected from each of the 3 piezometers. Temperature, pH, and Eh were measured on site using a Hydrolab™ multi-parameter probe.

2.4 Bulk Chemistry Analysis

Two cores were collected from Hubbard-Murphree Reservoir for bulk elemental analysis. Cores 2D and 3D were cut in half lengthwise with a circular saw and sampled at 2-cm intervals. The blade was set at a depth of 0.32 cm to ensure that metal shavings would not penetrate the sediment very deeply. After the top half of the tubing was removed the sediment was split lengthwise with a plastic putty knife. The sides of the sediment were cut away and discarded to prevent contamination from the metal shavings produced by the saw (Figure 7). Samples were

dried at 75° C for 48 hours in a forced air oven then crushed and passed through a 200-mesh sieve.

Following crushing and sieving, the sediment samples were prepared for analysis utilizing the acid digestion procedure described by Bernas (1968). This procedure involved placing 50 mg of crushed sediment into an acid digestion vessel with hydro-fluoric, nitric, and hydro-chloric acids. The mixture was then heated in an oven at 110° C for 40 minutes. Following heating, the solution was allowed to cool. Finally, 2 g of boric acid was added and the solution was standardized to 100 mL by adding deionized water. The prepared aqueous samples were then analyzed for a suite of elements by

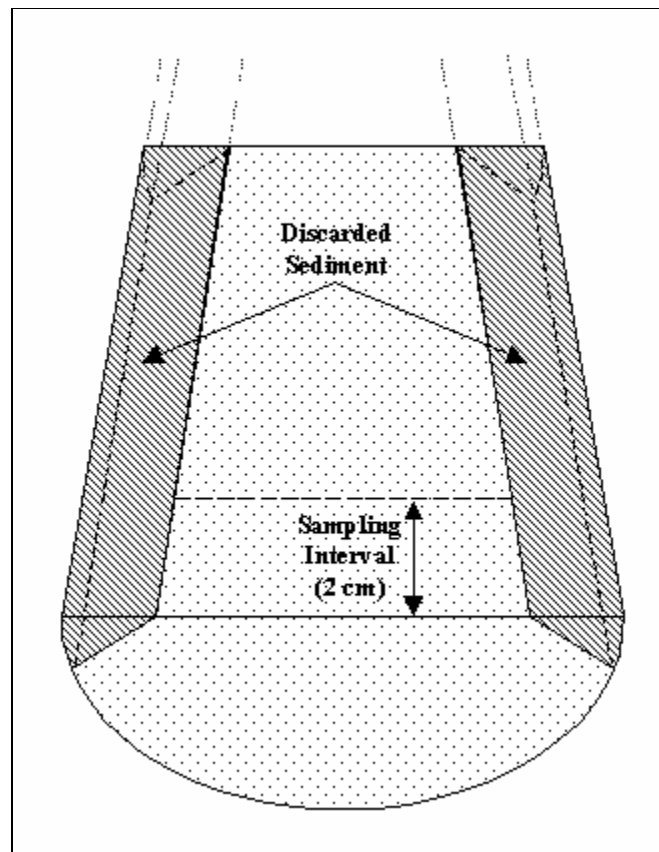


Figure 7. Cross-section of core after splitting. The sediment edges were removed to avoid contamination from the metal shavings produced by the circular saw.

optical emission inductively coupled plasma (ICP) spectrometry. These analyses provided a means of determining which elements were present in the lake sediment and at what concentrations.

2.5 Leaching Experiments

The effects of atmospheric exposure on the sediments at Hubbard-Murphree Reservoir was investigated using three horizons in each of two cores from the reservoir for leaching experiments. The horizons were from upper, middle, and lower sections of Cores 2E and 3E collected from the reservoir (Figure 8). Some of these leaching experiments were conducted using an N₂-atmosphere glove bag as a way to simulate a reducing environment and some were conducted under standard atmospheric conditions.

Sediment samples were homogenized and split into two 20-g sub-samples. Each split was then mixed with 800 mL of deionized water and kept in suspension using a magnetic stirrer for up to 80 hours. Deionized water used in the reducing environment was boiled prior to use in order to purge it of any dissolved oxygen. An oxygen absorbent was placed in the glove bag during the experiments to absorb any residual oxygen in the chamber. One sample from each pair was mixed in the reducing environment and the other was mixed under standard atmospheric conditions (no glove bag).

Aqueous samples were extracted from the slurries at regular intervals. The sampling frequency was approximately logarithmic. 10 to 12 mL samples were collected with a syringe, immediately filtered through 0.45- μ m cellulose acetate filters, and treated with a drop of concentrated nitric acid. Redox potential was recorded at 5-minute intervals for the duration of each leaching experiment. pH was recorded every time a sample was collected. The initial and

final volume of the slurry was recorded so that water losses to evaporation, which would affect the concentrations of dissolved species, could be compensated for.

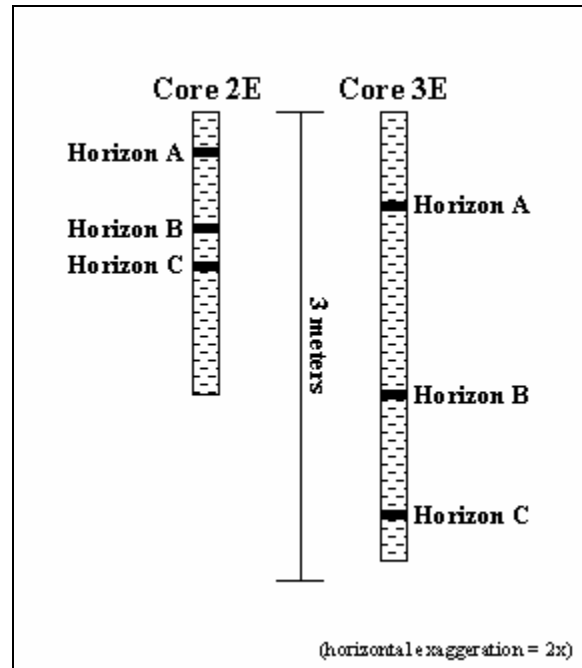


Figure 8. Illustration of the sampling horizons used in the leaching experiments.

CHAPTER 3

RESULTS

3.1 Site Characterization

3.1.1 Redox Potential

Manual redox potential measurements made on Cores 1A-6A were collected over time periods ranging from 3 to 5.5 hours. The manual method was the first attempt at quantifying the Eh as a function of depth in the cores. A voltmeter was attached to the electrodes and when the voltage readout became stable, a measurement was recorded. Figure 9 illustrates Eh vs. time at a depth of 0.5 meters in Core 6A. The sampling interval was 30 minutes. Discerning an obvious equilibration point based on this data was not possible. It is suspected that the jostling of the probe each time the meter was connected prevented equilibration between the electrode and sediment from taking place. However, though equilibration may not have occurred, redox potential measurements were recorded and plotted to see if there were any trends with depth. It is theorized that though the redox potential values themselves may be inaccurate (falsely high), the error resulting from the probes not equilibrating is applied uniformly and the “redox potential vs. depth” trends observed in the manually collected data are at least qualitatively accurate.

A data logger was used to record redox potential measurements of Cores 1C-4C. The data logger method was the second attempt at quantifying the Eh in the cores. Measurements were made over time periods ranging from 9 to 47 hours. Figure 10 illustrates Eh vs. time at a depth of 0.5 meters in Core 3C. The sampling interval was 5 minutes. Electrode equilibration was assumed to have taken place when the Eh values became relatively steady. The in situ Eh value

of the sediment at a given depth in a core was interpreted to be the value observed immediately following equilibration. The continued gradual drop in Eh following equilibration is the result of continued oxidation of organic matter in the core.

The measured redox potential of the sediment in Cores 1A-6A varied between 175 mV and -325 mV (a range of approximately 500 mV) (Figure 11). A trend of increasing Eh with depth was observed in some of the cores (most noticeably in Cores 3A and 4A), a phenomenon suspected to be caused by upwelling groundwater beneath the lake.

The measured redox potential of the sediment in Cores 1C-4C varied between approximately 25 mV and -525 mV (Figure 12). The trend of increasing Eh with depth is not as pronounced in these measurements. Also, the range in redox potential readings is wider, at approximately 550 mV, and both the minimum and maximum values were significantly lower.

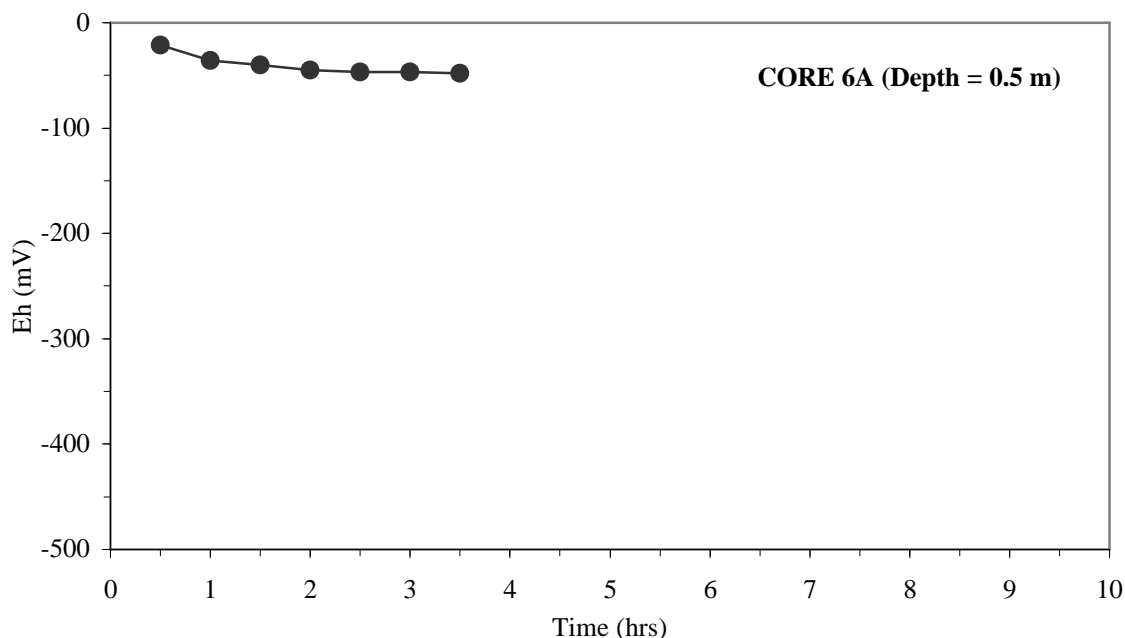


Figure 9. Eh as a function of time, using manually collected data, at a depth of 0.5 meters in Core 6A.

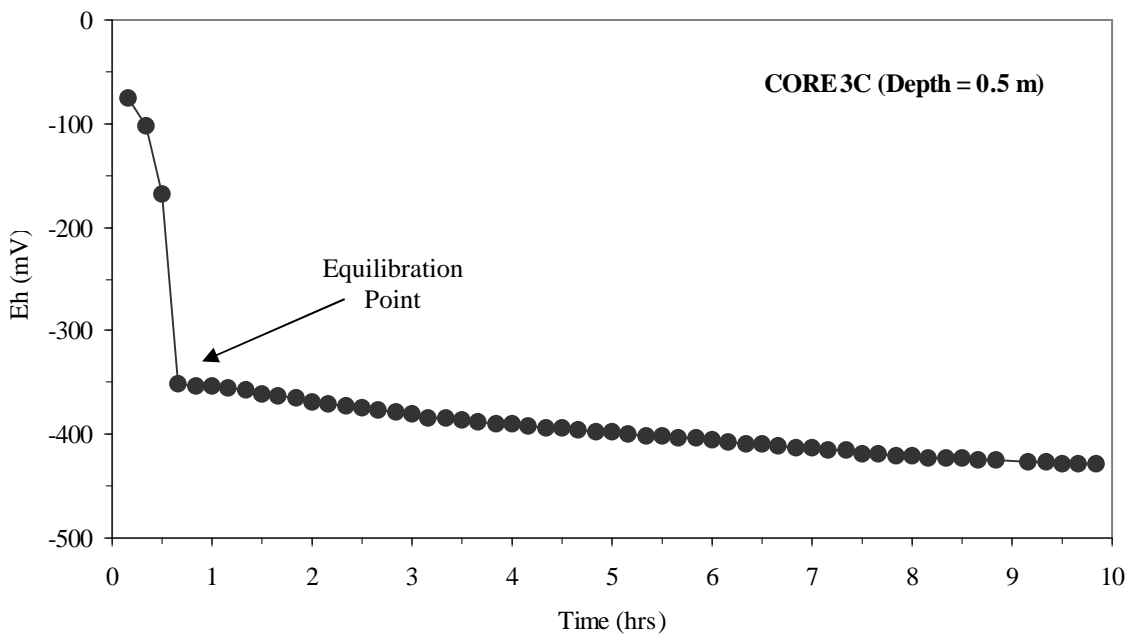
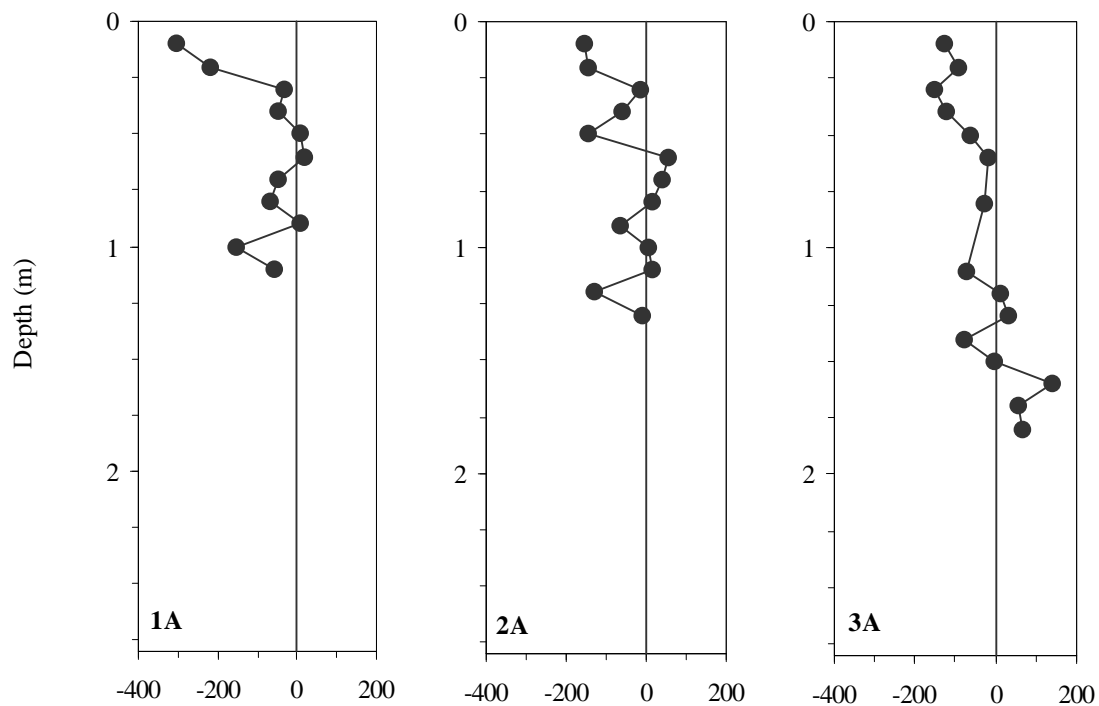


Figure 10. Eh as a function of time, using a data logger, at a depth of 0.5 meters in Core 3C.



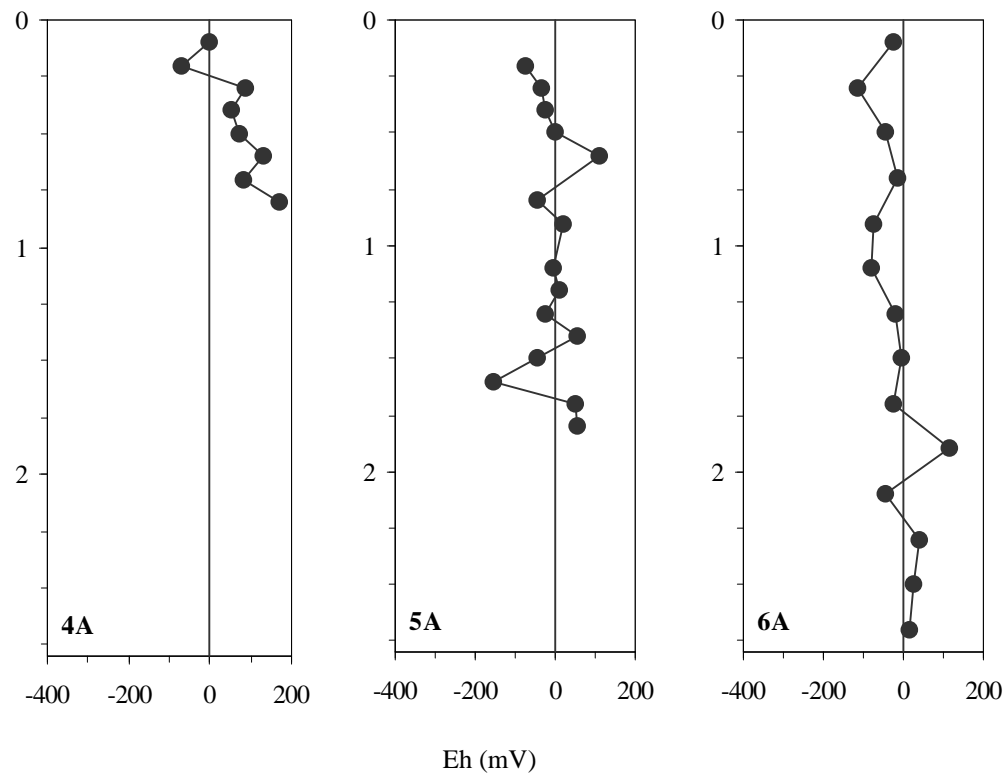
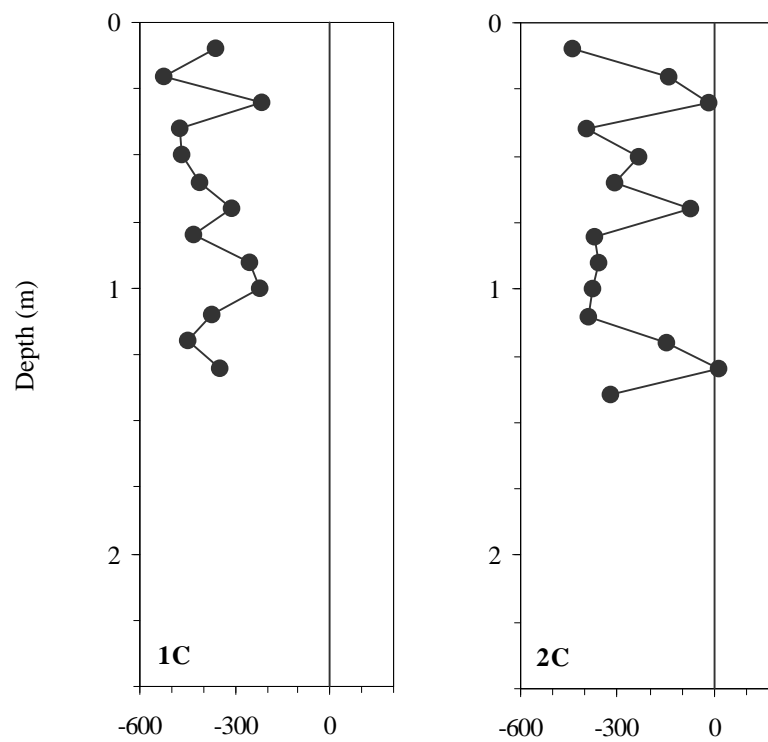


Figure 11. Eh vs. depth (collected manually) in the cores obtained from Hubbard-Murphree Reservoir during the May, 2001 coring trip.



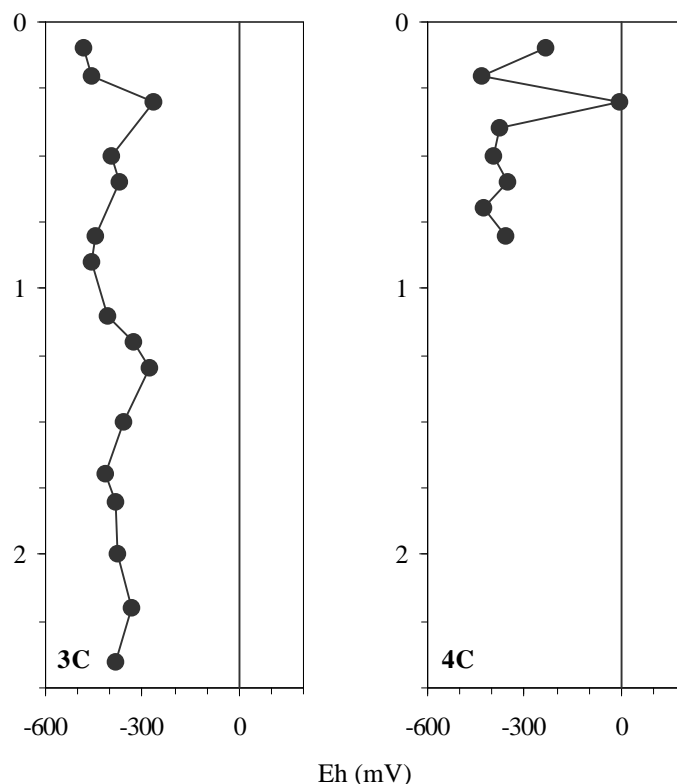


Figure 12. Eh vs. depth (collected with a data logger) in the cores obtained from Hubbard-Murphree Reservoir during the August, 2001 coring trip.

3.1.2 Piezometer Data

Water levels obtained from measurements taken in November 2001 indicated that the water level was highest in the deepest piezometer, followed by the middle then shallowest piezometers (Table 2, Figure 13). Redox potential values obtained from measurements made in August 2002, of the water in each column, ranged between 11 and 55 mV. The pH of the water ranged between 5.5 and 6.7. pH was highest in the shallow piezometer and lowest in the deep piezometer.

Little variation in aqueous concentration with depth was observed among the 9 elements detected in the samples. However, Ca, Cu, K, Na, and Sr did exhibit slight general trends of increasing or decreasing concentration with depth (Figure 14). Ba, Fe, Mg, Mn, and Zn exhibited no significant trends (Figure 15).

Table 2. Water level and redox potential measurements from each of the 3 piezometers in the piezometer nest. The screened interval of each piezometer is 0.15 m in length.

Depth Below Sediment/Water Interface (m)	Water Level (height above lake surface) (m)	Eh (mV)	pH
0.91	0.075	11	6.7
1.52	0.2	31	6.5
2.13	0.34	55	5.5

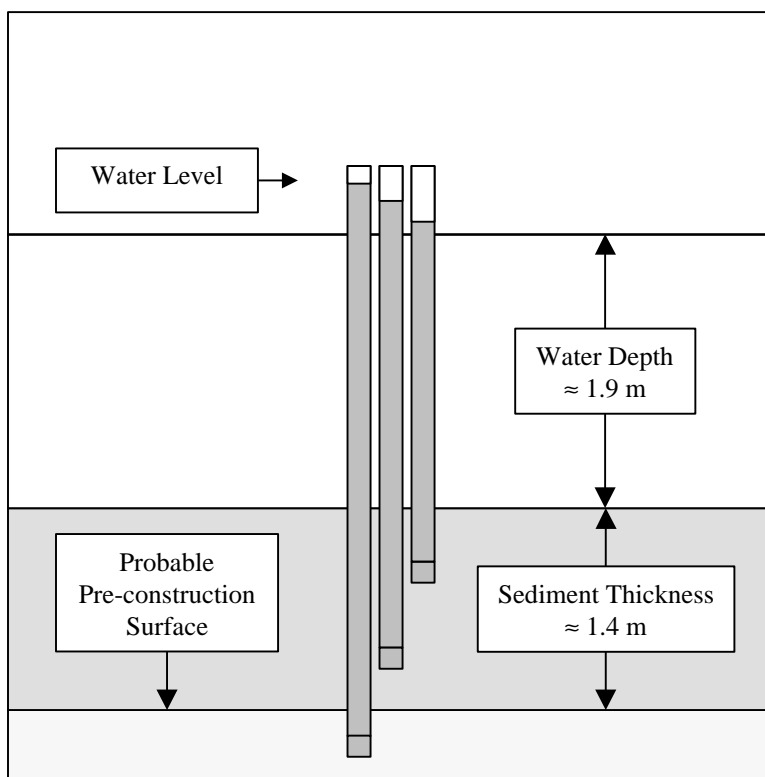


Figure 13. Illustration of the water level in each of the piezometers, as well as approximate sediment thickness and water depth at the piezometer nest location (not to scale).

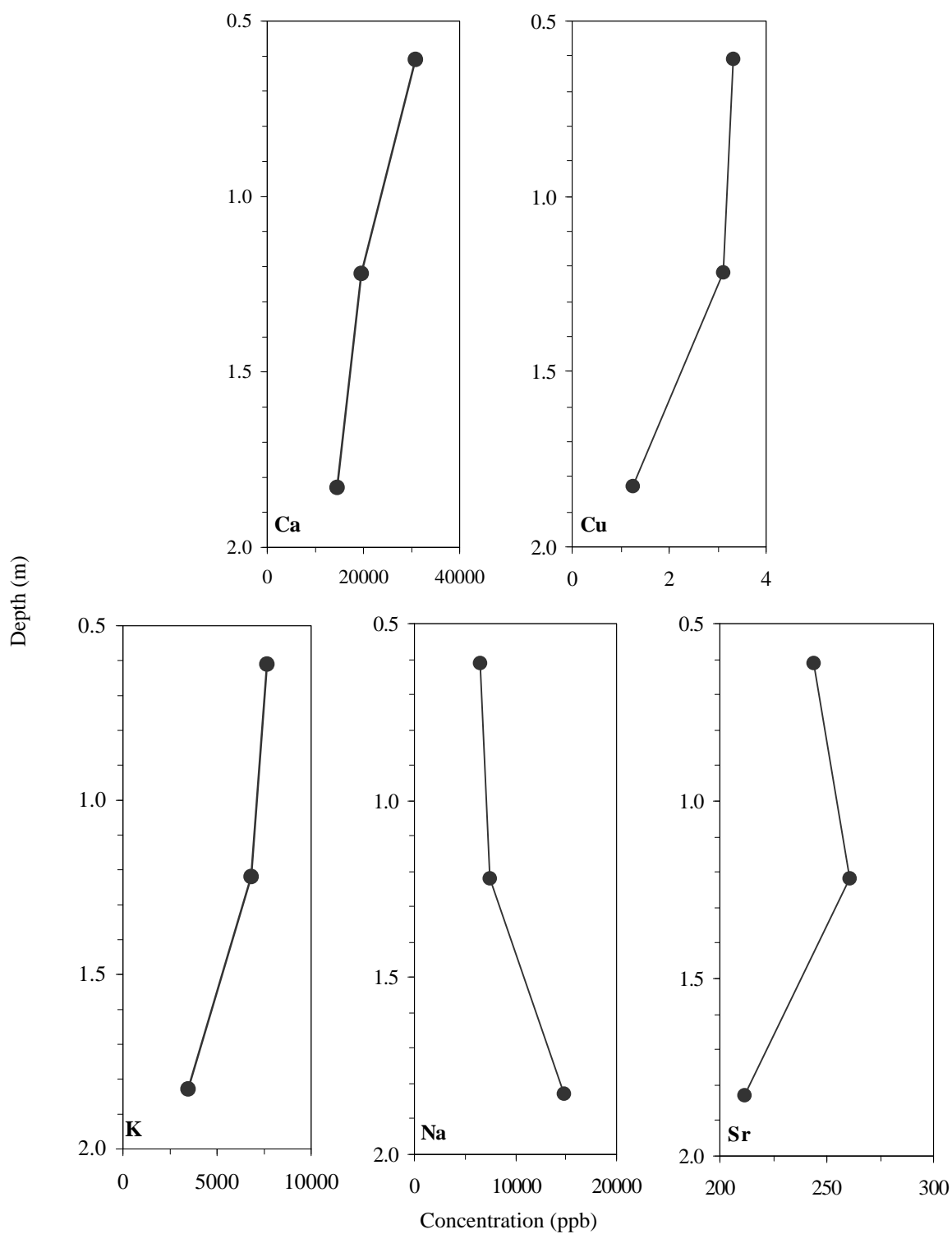


Figure 14. Select elemental analysis results (Ca, Cu, K, Na, and Sr) from pore water samples collected from the piezometers installed at Hubbard-Murphree Reservoir.

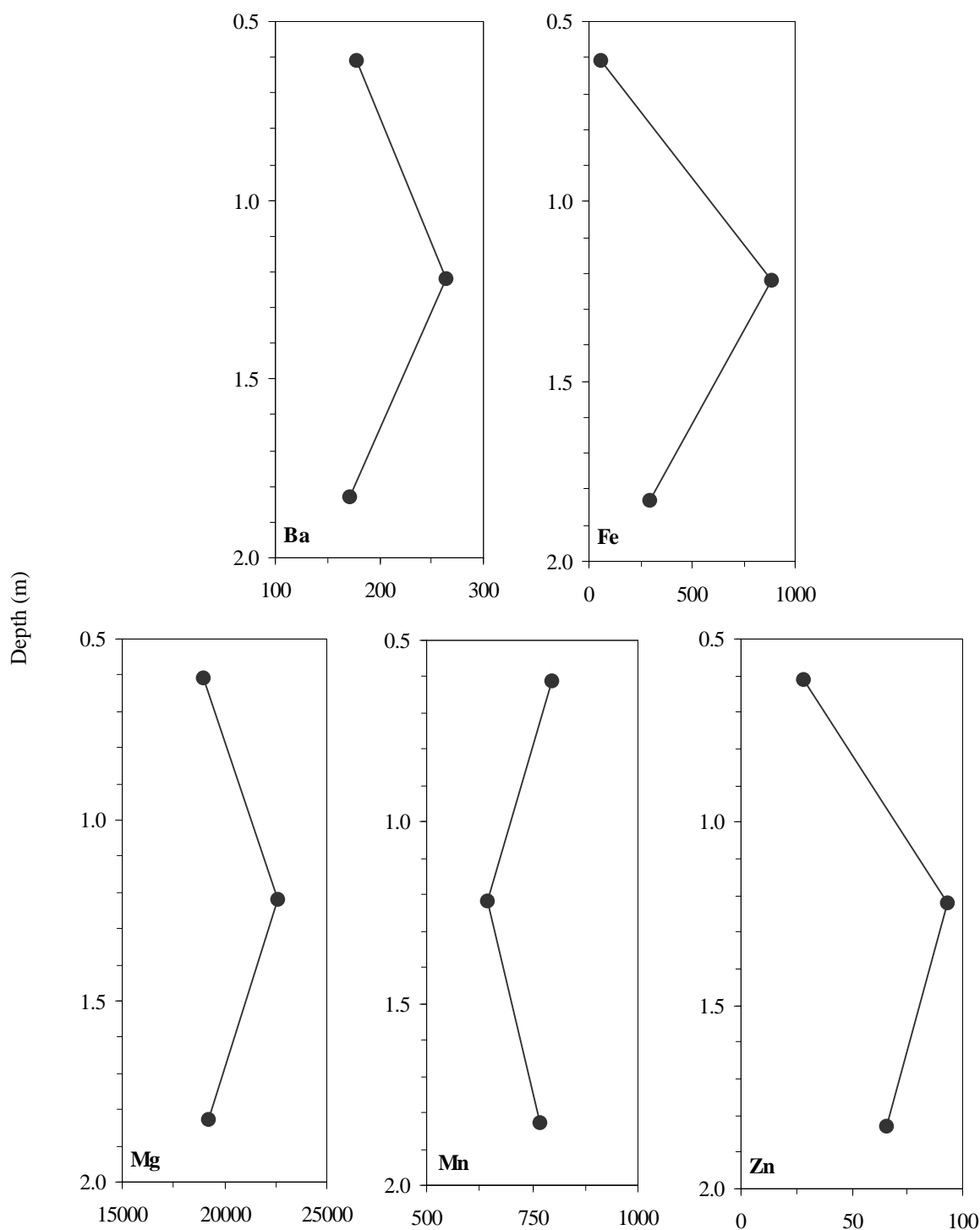


Figure 15. Select elemental analysis results (Ba, Fe, Mg, Mn, and Zn) from pore water samples collected from the piezometers installed at Hubbard-Murphree Reservoir.

3.1.3 Bulk Chemistry

Table 3 lists the 26 elements analyzed for and the bulk chemistry instrument detection and reporting limits for each (reporting limit = 5 x detection limit). Of these elements, 11 were detected in Cores 2D and 3D (Figures 16-18, 20-25, 27, and 28). Copper and nickel were only detected in Core 3D (Figures 19 and 26).

Several elements show variability in concentration with depth. All elements, with the exception of Na and Zn, decrease in concentration in the bottom 50 cm in Core 2D. Na and Zn both increase in concentration over the same interval. Element concentrations vary little with depth above this interval. Core 3D does not show the same variation in concentration over its bottom 50 cm. However, there is an interval (1.6 – 2.0 m) that shows a slight decrease in concentration for some elements (e.g. Al, Fe, Li, and Mg). Ca, Na, and Sr, exhibit a slight increase in concentration over the length of both cores. Al and Fe exhibit a slight decrease in concentration over the length of Core 2D.

Table 3. Summary of detected and undetected elements in the bulk chemistry analysis, as well as the instrument bulk-chemical detection and reporting limits for each.

Detected Elements			Undetected Elements		
Element	Detection Limit (mg/Kg)	Reporting Limit (mg/Kg)	Element	Detection Limit (mg/Kg)	Reporting Limit (mg/Kg)
Al	57	286	Ag	14	70
Ba	8	40	As	100	500
Ca	20	100	B	11	57
Cu	19	97	Be	1.4	7
Fe	9.2	46	Cd	5.4	27
K	480	2400	Co	14	70
Li	12	62	Cr	14	71
Mg	3.2	16	Mo	16	79
Mn	2.8	14	P	152	760
Na	138	690	Pb	84	420
Ni	30	150	Sb	64	320
Sr	0.8	4	Se	150	750
Zn	12	59	Ti	5.6	28

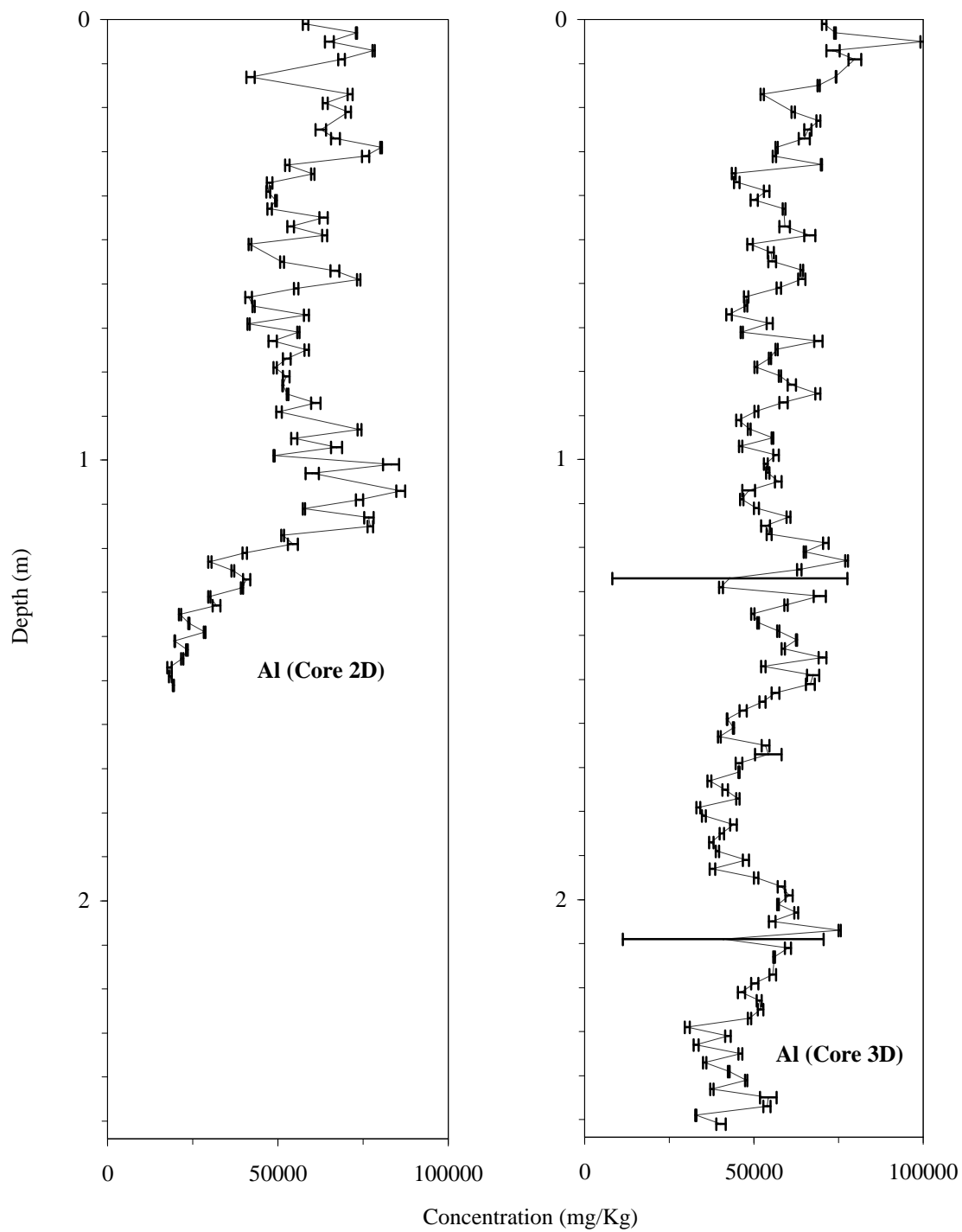


Figure 16. Al concentrations in Cores 2D and 3D. Concentrations are expressed as error bars.

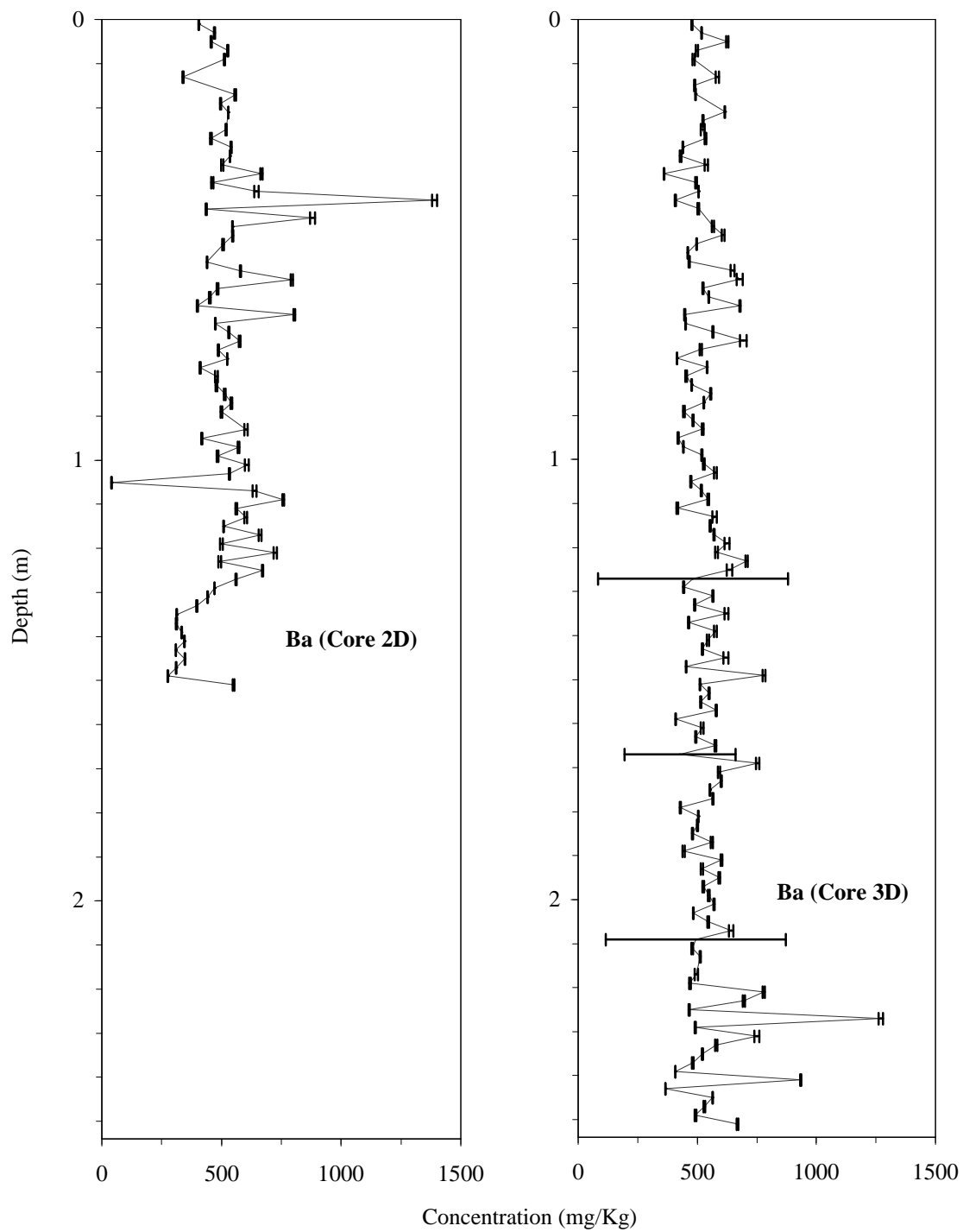


Figure 17. Ba concentrations in Cores 2D and 3D. Concentrations are expressed as error bars.

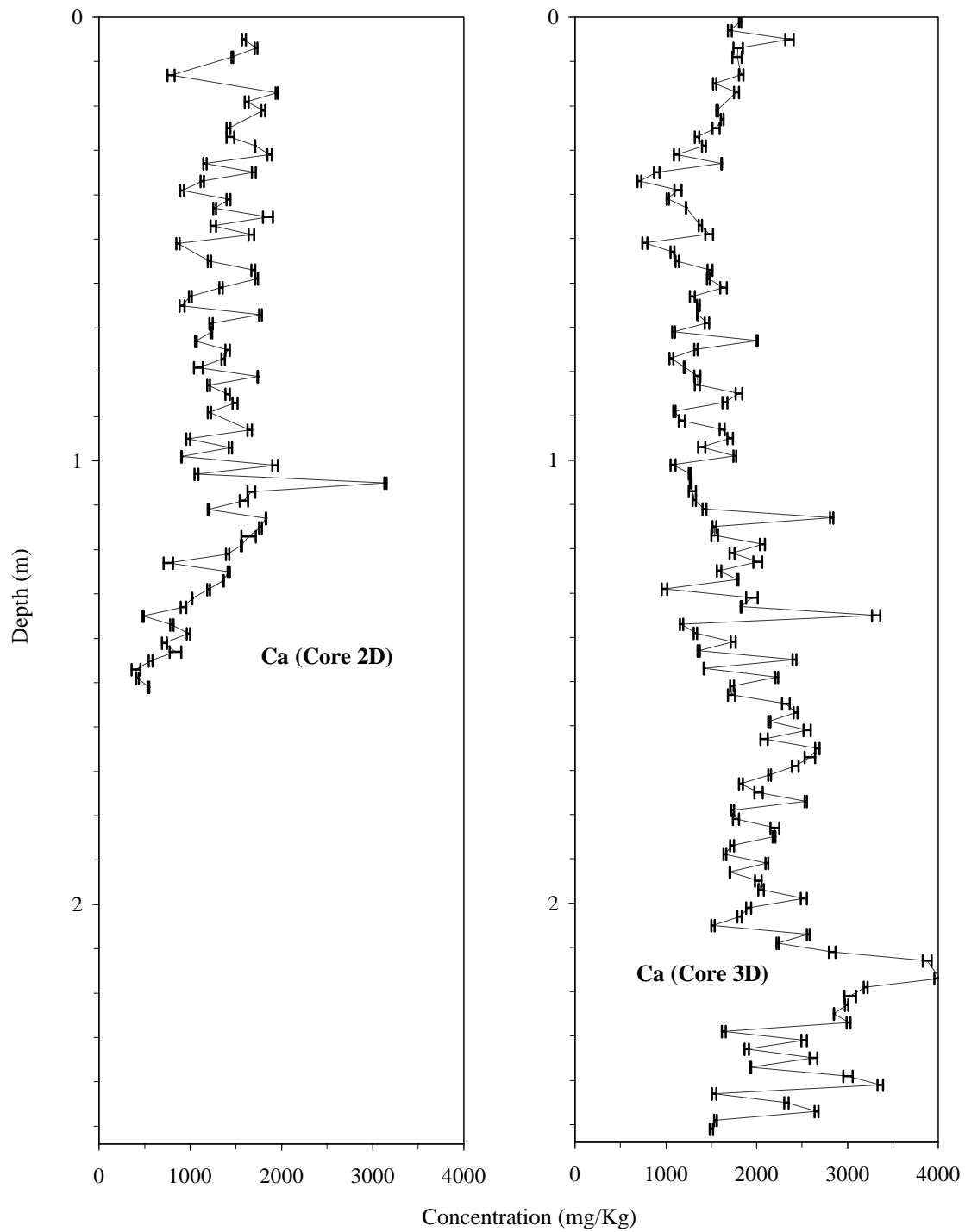


Figure 18. Ca concentrations in Cores 2D and 3D. Concentrations are expressed as error bars.

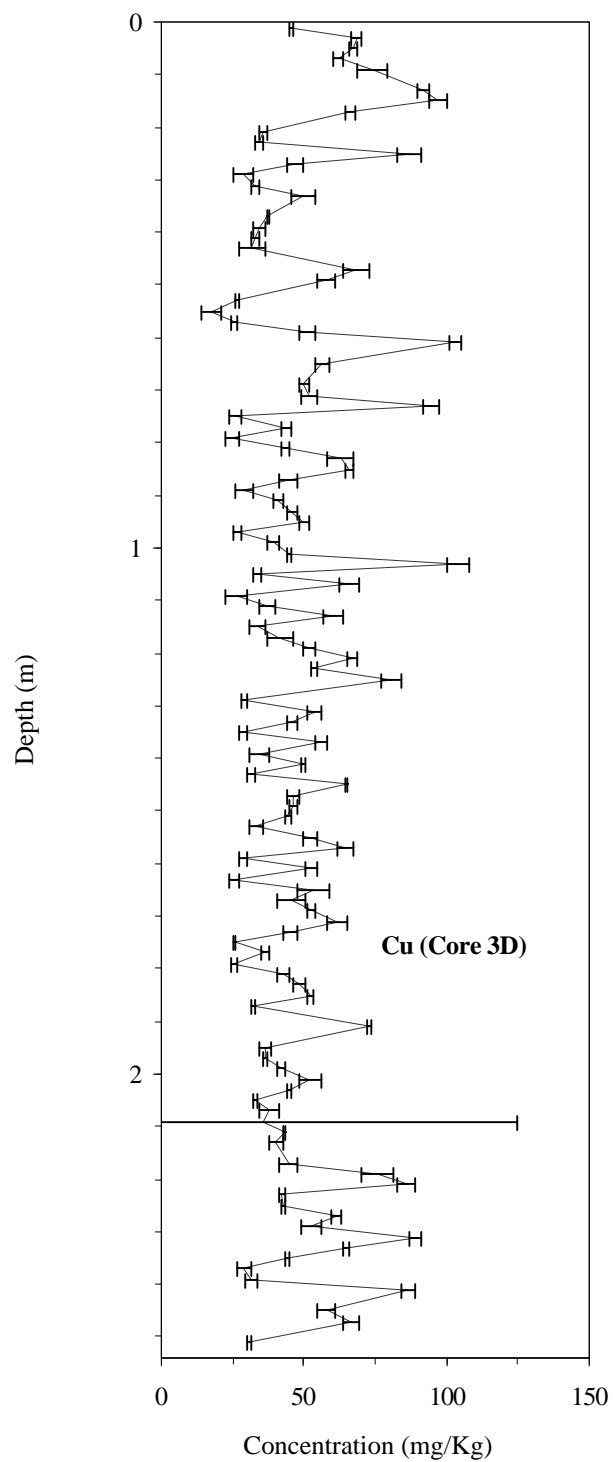


Figure 19. Cu concentrations in Core 3D. Concentrations are expressed as error bars.

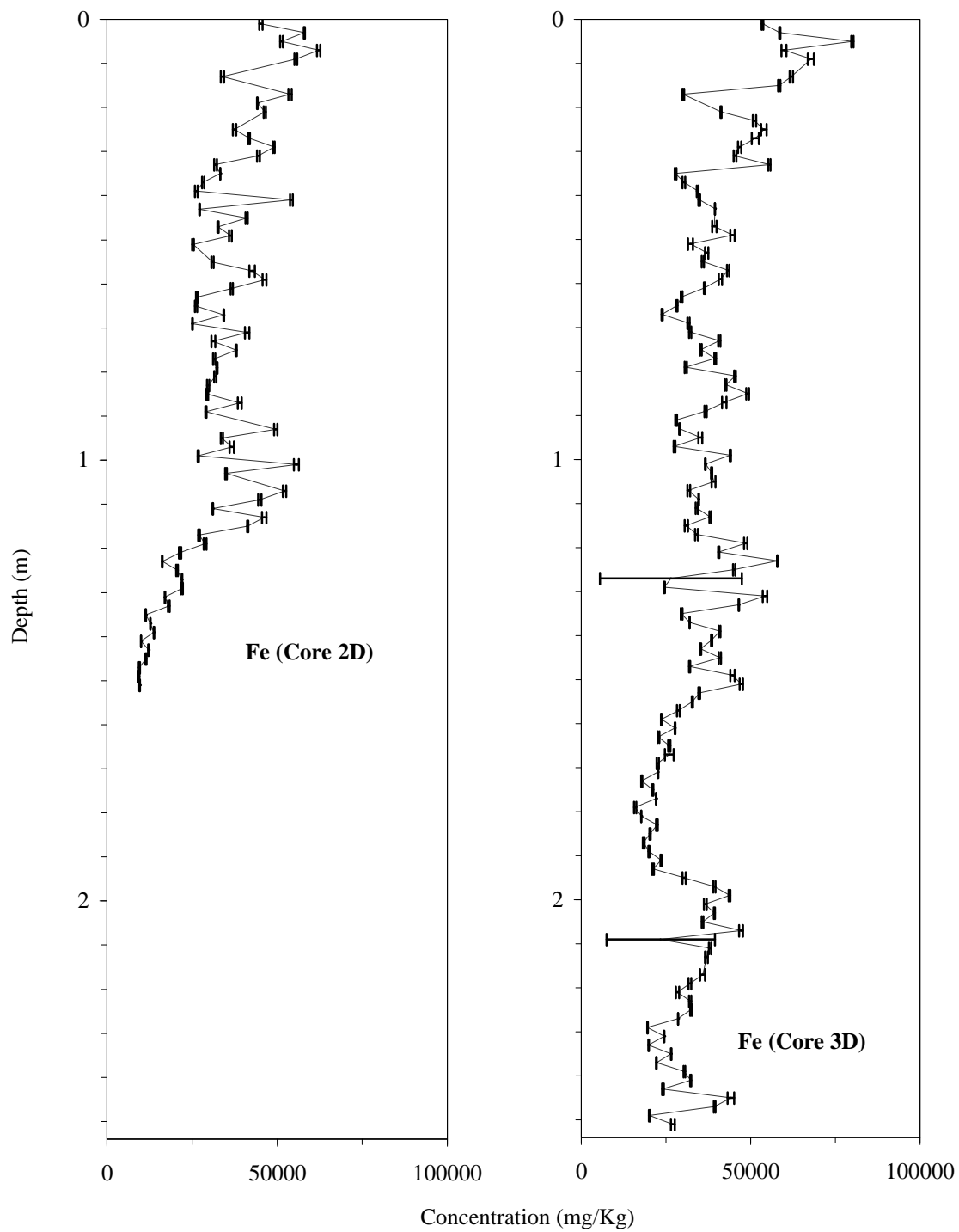


Figure 20. Fe concentrations in Cores 2D and 3D. Concentrations are expressed as error bars.

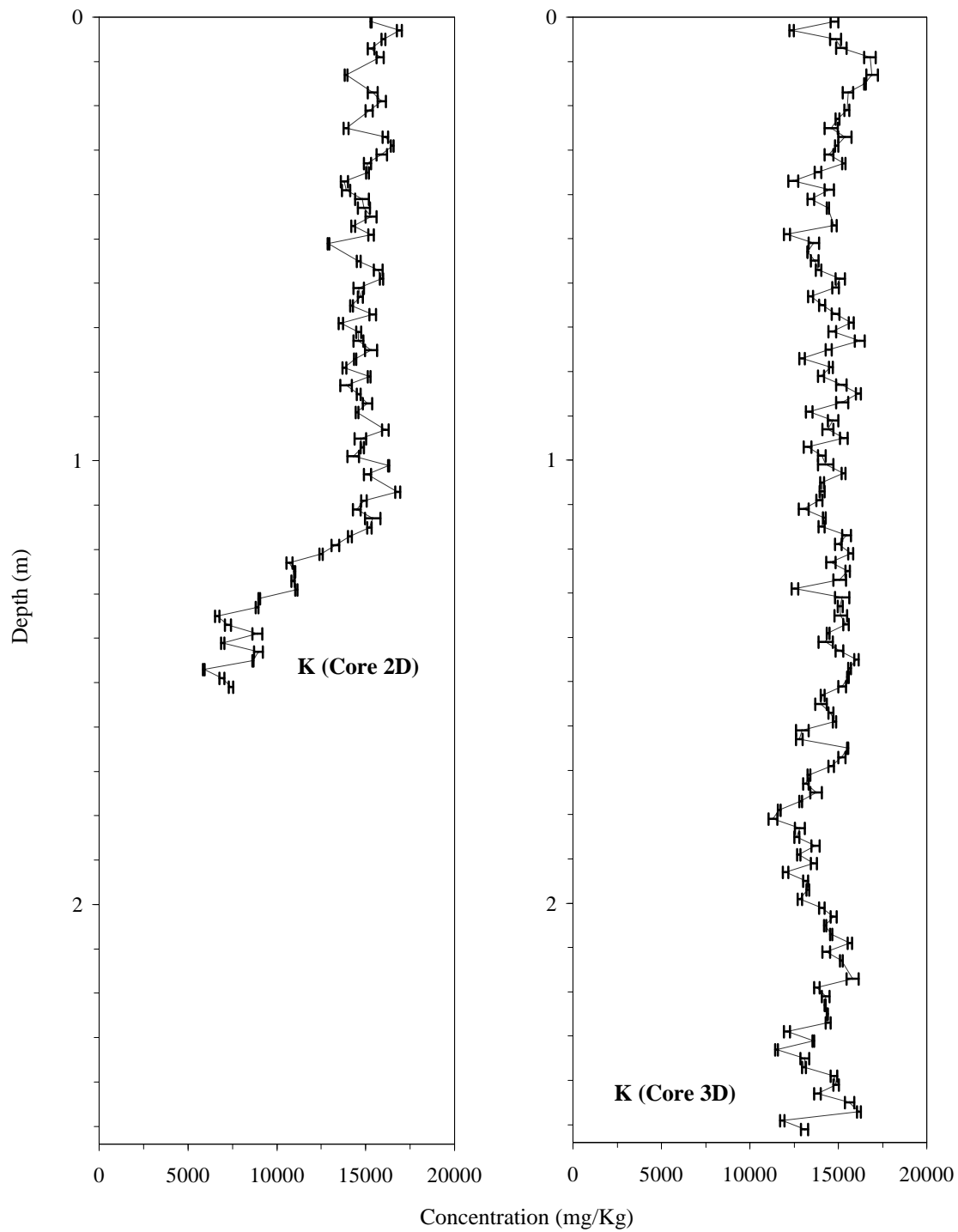


Figure 21. K concentrations in Cores 2D and 3D. Concentrations are expressed as error bars.

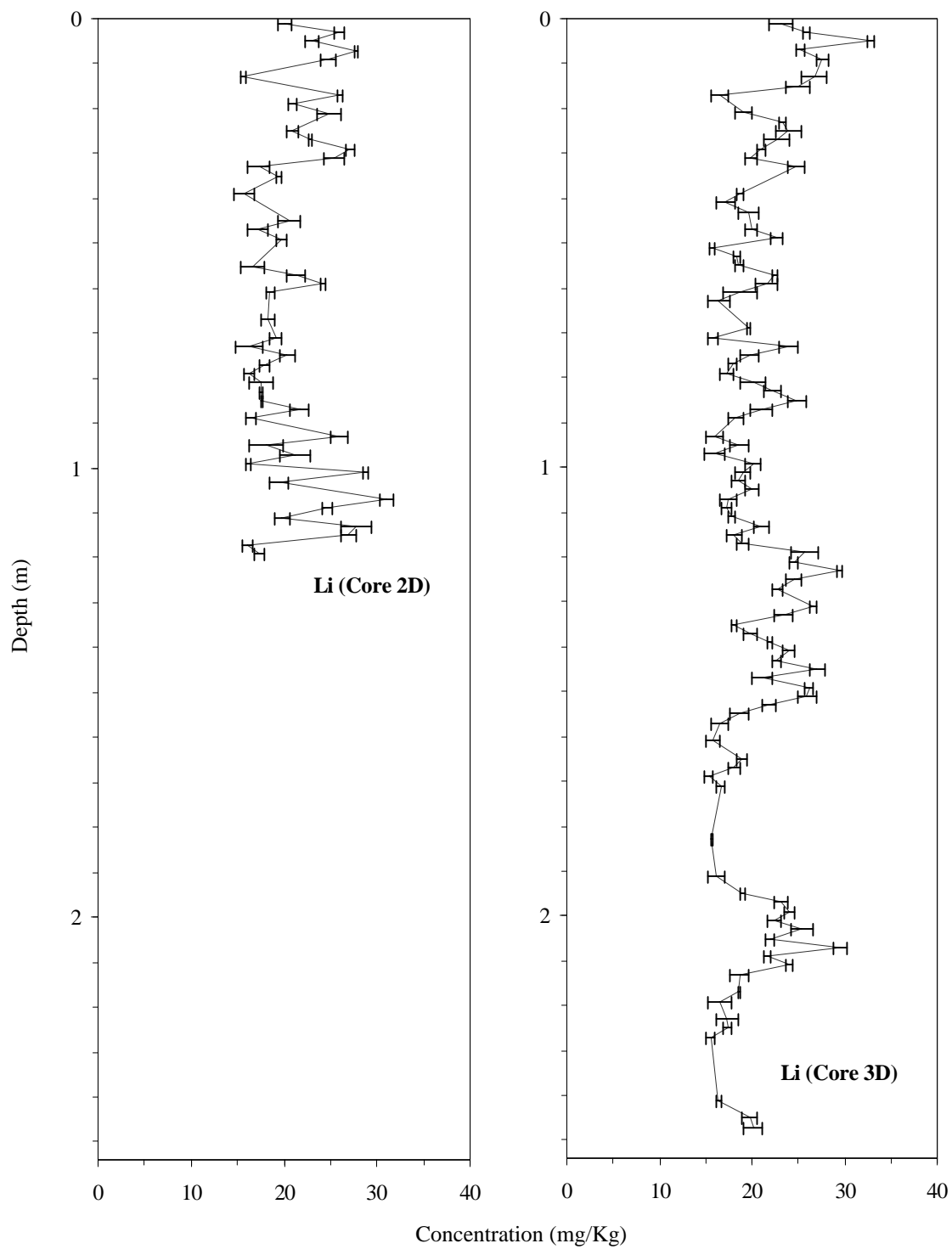


Figure 22. Li concentrations in Cores 2D and 3D. Concentrations are expressed as error bars.

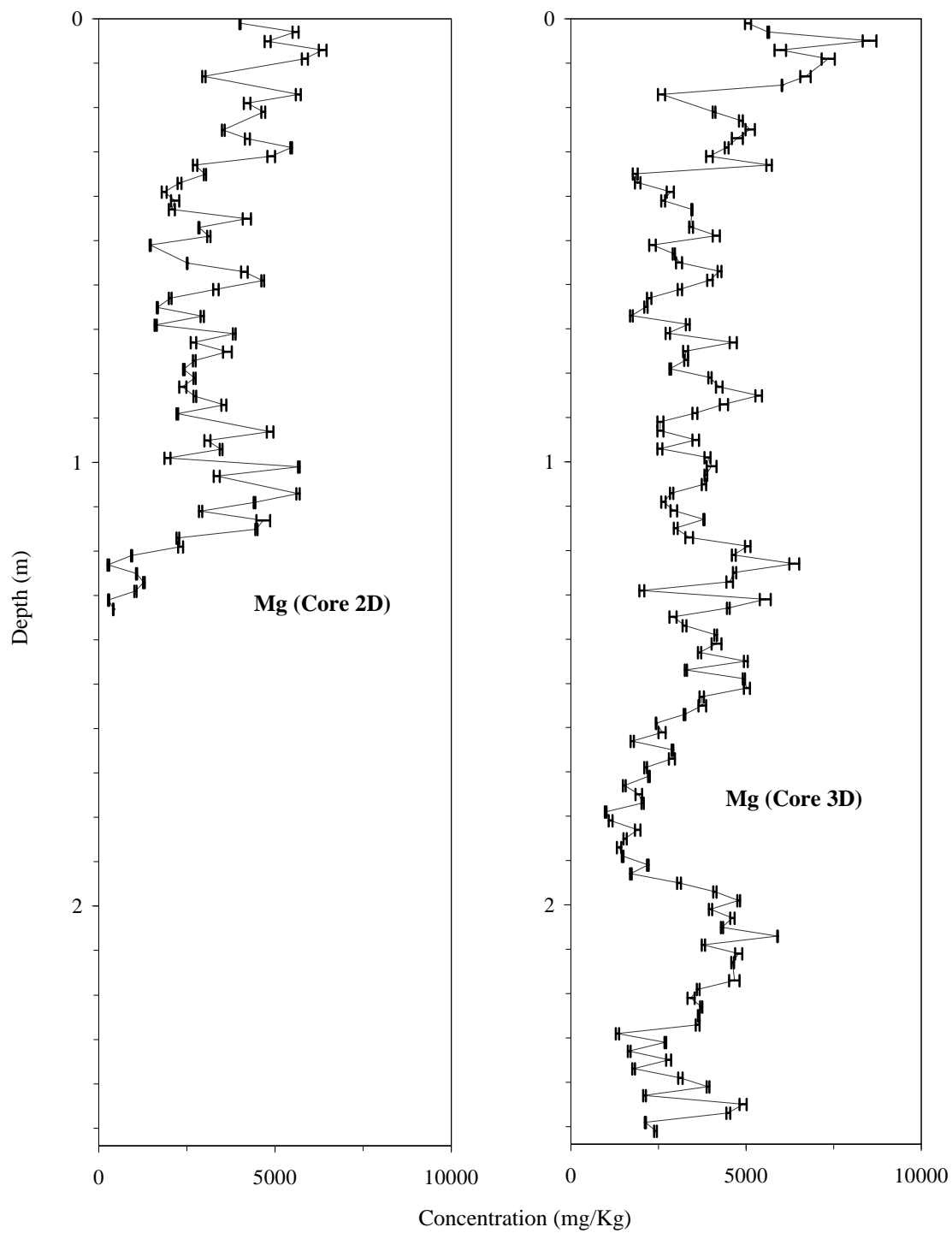


Figure 23. Mg concentrations in Cores 2D and 3D. Concentrations are expressed as error bars.

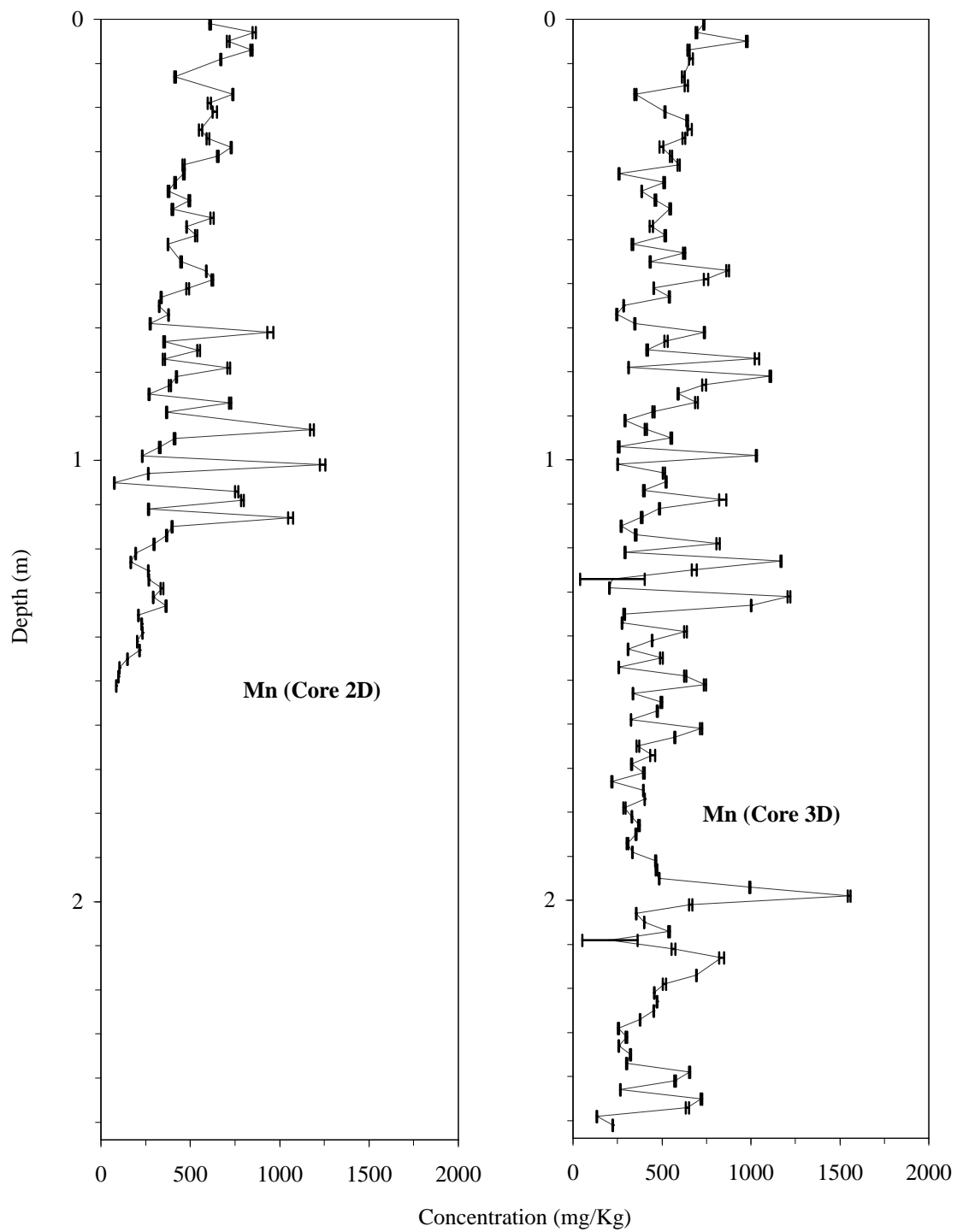


Figure 24. Mn concentrations in Cores 2D and 3D. Concentrations are expressed as error bars.

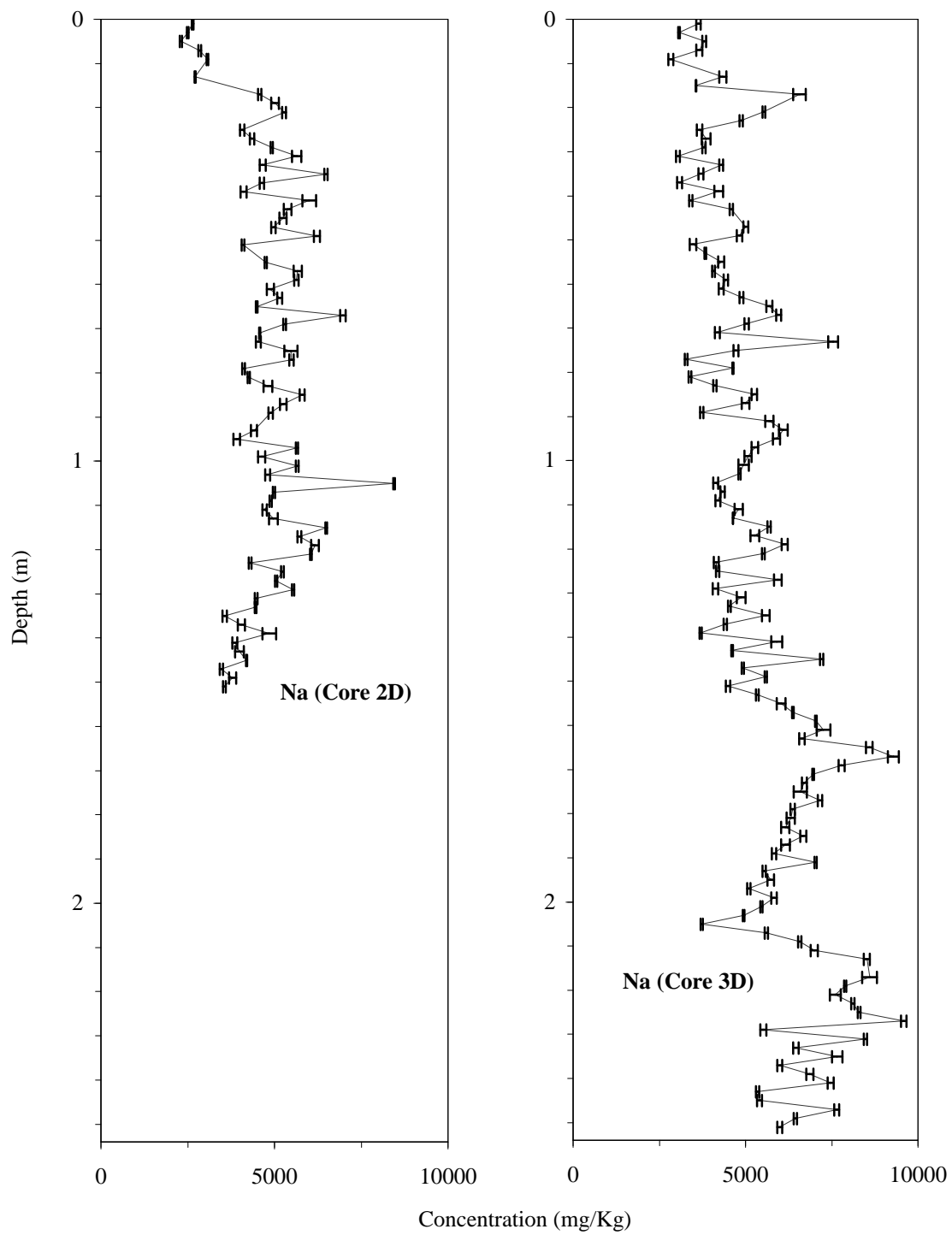


Figure 25. Na concentrations in Cores 2D and 3D. Concentrations are expressed as error bars.

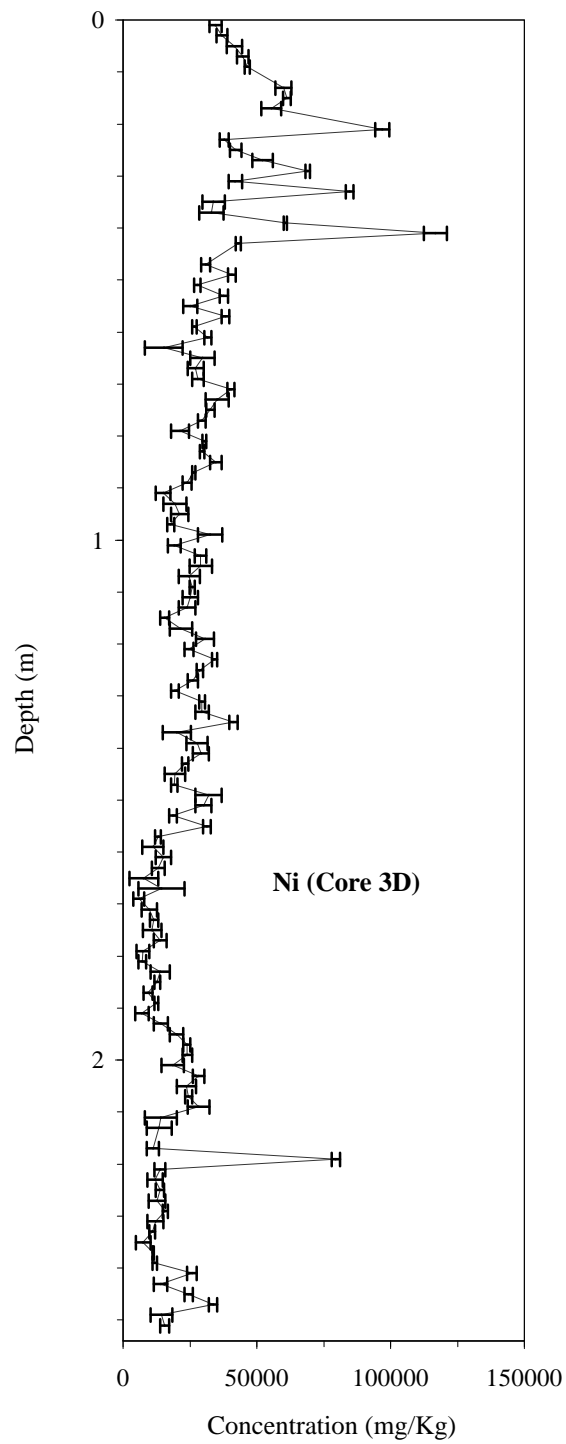


Figure 26. Ni concentrations in Core 3D. Concentrations are expressed as error bars.

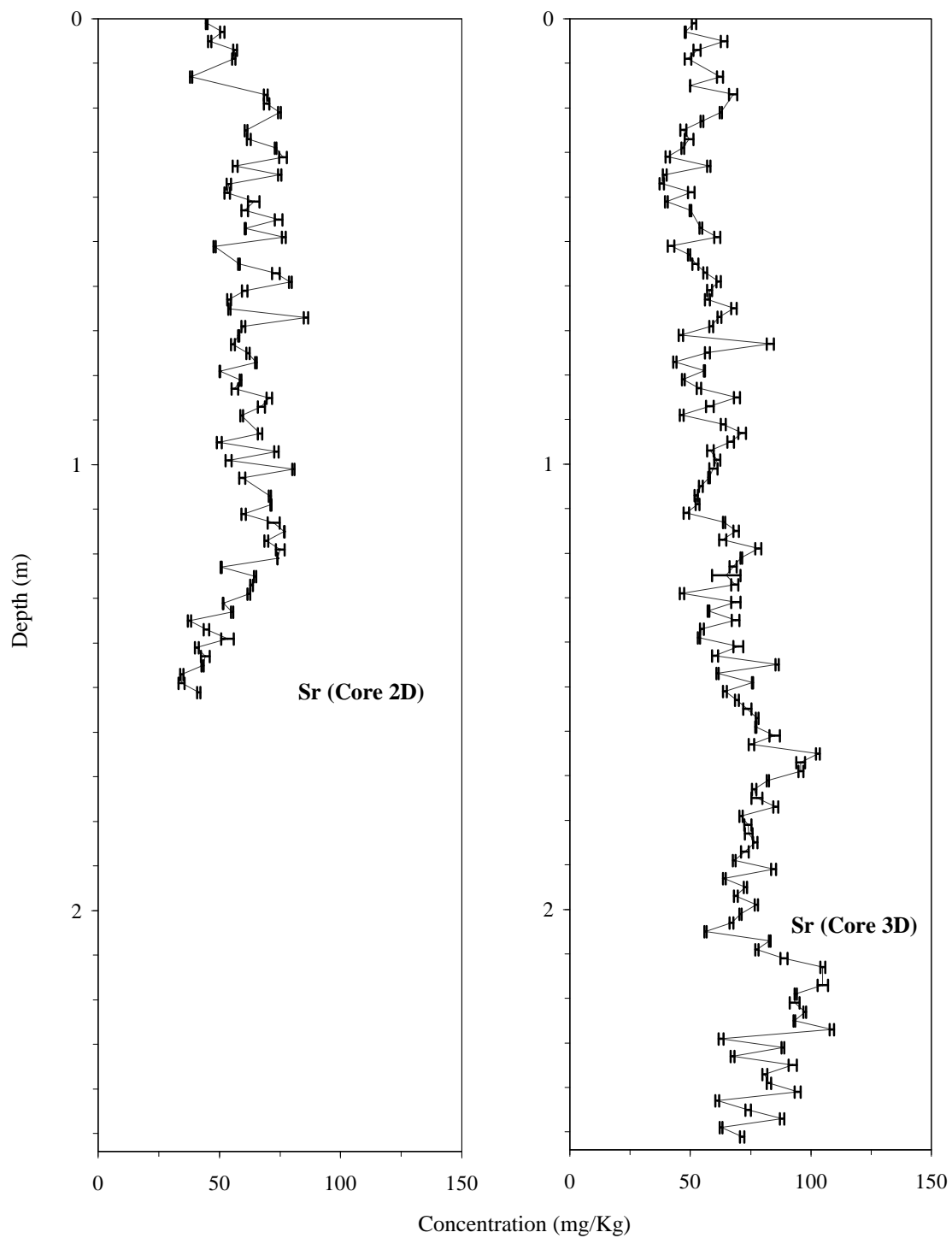


Figure 27. Sr concentrations in Cores 2D and 3D. Concentrations are expressed as error bars.

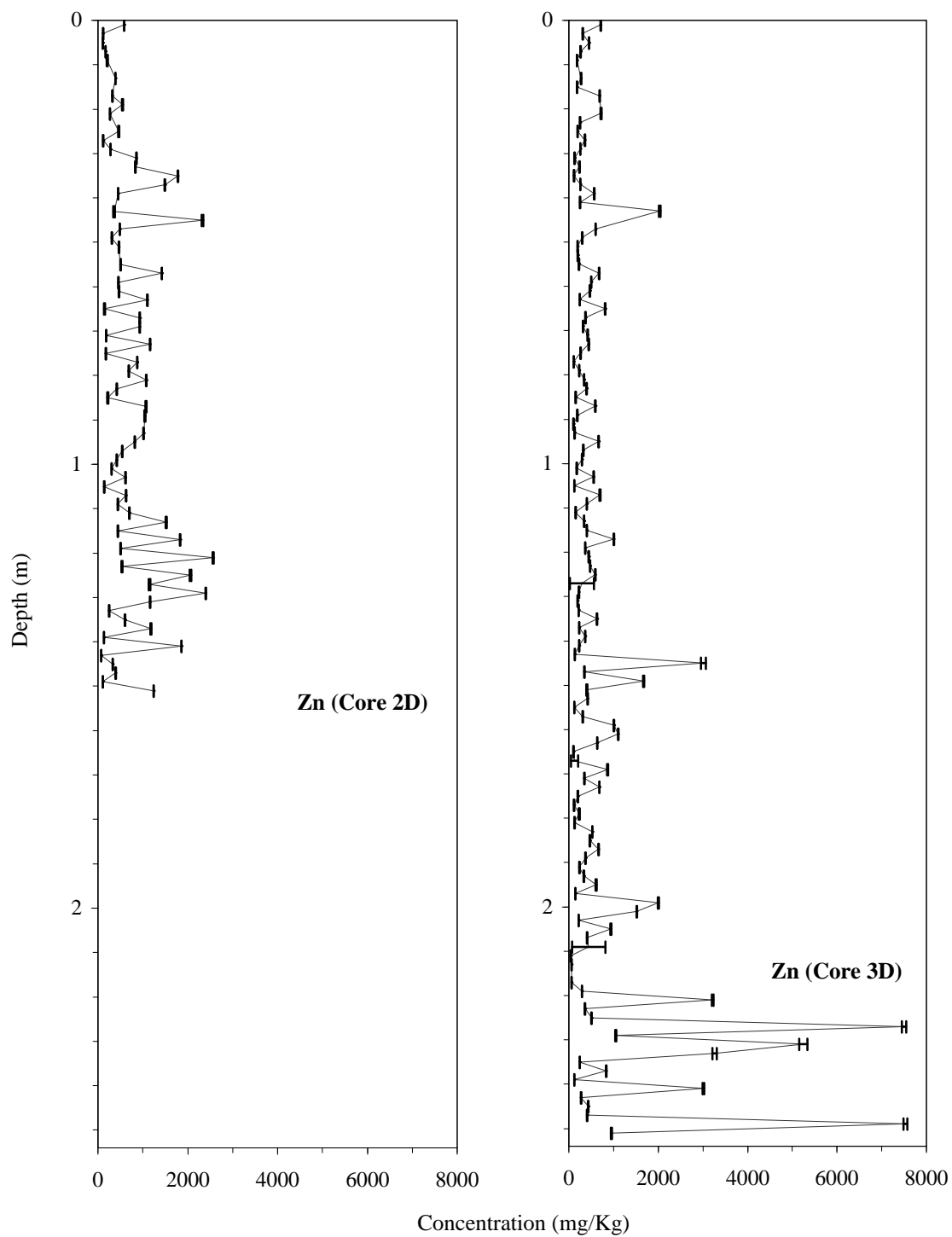


Figure 28. Zn concentrations in Cores 2D and 3D. Concentrations are expressed as error bars.

3.2 Leaching Experiments

Results from each of the leaching experiments were fairly consistent. The same elements were detected in each of the leaching slurries with the exceptions of Ba, which was not detected in leachate from Core 3E: Horizon B, and Li, which was only detected in leachate from Core 3E: Horizons A and C (Table 4). Table 4 also lists the aqueous detection and reporting limits for each of the detected elements. The concentrations of most detected elements under reducing conditions were consistently, and in some cases significantly, higher than concentrations of elements under oxidizing conditions.

The first three leaching experiments were run for 48, 22, and 24 hours on Core 3E: Horizons A, B, and C respectively. The results of these experiments suggested that more time was needed to establish trends of any significance. Also, an observed pattern of increasing concentration over time suggested that evaporation losses might have affected the results. Therefore, the last three leaching experiments (Core 2E: Horizons A, B, and C) were conducted for longer time periods (up to 80 hours) and the initial and final volumes were recorded so corrections for evaporation could be made. The results from these 3 experiments should be considered the most reliable. Figure 29 illustrates the effect evaporation had on the leaching slurry of Horizon C in Core 2E. Evaporation was causing a false increase in concentration. The evaporation correction is based on the initial and final volume of the slurry. By making note of the amount of sample extracted at each sampling time it is possible to calculate a projected final volume. Any discrepancy between the projected final volume and actual final volume was attributed to evaporation losses.

Table 4. Summary of detected elements in each of the leaching experiments and the aqueous chemical detection and reporting limits for each.

Elements Detected	Detection Limit (ppb)	Reporting Limit (ppb)	Core 2E			Core 3E		
			Horizon A	Horizon B	Horizon C	Horizon A	Horizon B	Horizon C
Al	29	143	X	X	X	X	X	X
Ba	4	20	X	X	X	X		X
Ca	10	50	X	X	X	X	X	X
Cu	10	49	X	X	X	X	X	X
Fe	4.6	23	X	X	X	X	X	X
K	240	1200	X	X	X	X	X	X
Li	6.2	31				X		X
Mg	1.6	8	X	X	X	X	X	X
Mn	1.4	7	X	X	X	X	X	X
Na	69	345	X	X	X	X	X	X
Ni	15	75				X	X	X
Sr	0.4	2	X	X	X	X	X	X
Zn	5.9	30	X	X	X	X	X	X

Redox potential and pH were monitored and recorded for the duration of each leaching experiment. The plots generated from this data indicate how reducing or oxidizing the conditions were for the duration of each experiment. Because the pH under reducing conditions and oxidizing conditions varied significantly, the Eh of each experiment was normalized to a pH of 7 to allow for a direct comparison. Figure 30 illustrates this normalization in one of the leaching experiments.

Figure 31 illustrates the change in redox potential over time in the leaching experiment of Core 2C: Horizon C. There are noticeable fluctuations in both the reducing and oxidizing slurries. However, this plot confirms that reducing and oxidizing conditions were maintained for the duration of the experiment. The redox potential difference between the reducing and oxidizing leaching experiments reached a maximum of approximately 325 mV. The Eh noise observed under oxidizing conditions is probably because the accuracy of redox potential measurements is diminished under oxidizing conditions (Faulkner et. al., 1989). Sharp decreases like those seen in the line representing reducing conditions in Figure 31 were caused by

mechanical problems. When stirring stopped due to slurry viscosity and water was stagnant for any length of time, a sharp decrease in redox potential was observed.

In the majority of the leaching experiments, elements exhibited initial significant fluctuations in concentration. This was followed by the development of distinct patterns with respect to concentration over time. These patterns are more visible in the experiments that were run for longer periods of time (e.g. Core 2E: Horizon C).

Figures 32-37 show the results from one of the horizons used in these experiments. Over the course of this leaching experiment Ca, Fe, Mg, Na, and Sr exhibited a significant general decrease in concentration over time under both reducing and oxidizing conditions (Figures 32-34). Also, elemental concentrations for these elements were higher under reducing conditions than under oxidizing conditions. Al, K, and Mn exhibited a significant general increase in concentration over time under both reducing and oxidizing conditions (Figures 35 and 36). K exhibited a much more significant increase in concentration under reducing conditions and a more moderate increase under oxidizing conditions. Ba, Cu, and Zn showed no significant patterns or variation in concentration over time under oxidizing or reducing conditions (Figures 36 and 37).

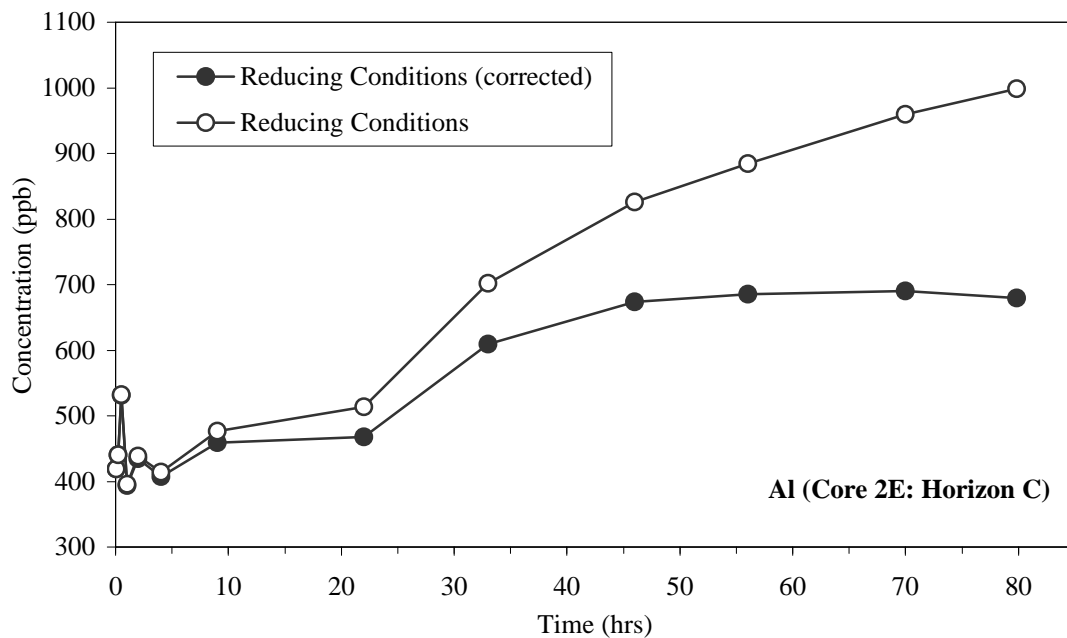


Figure 29. Al concentrations under reducing conditions in the Core 2E: Horizon C slurry, with and without evaporation correction.

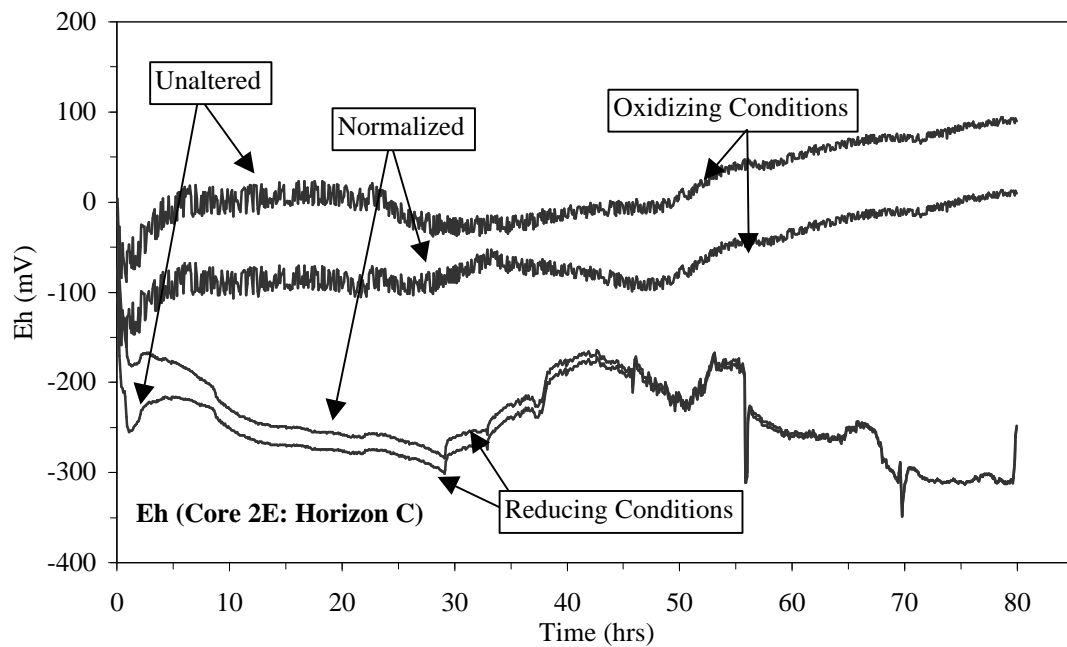


Figure 30. Unaltered Eh vs. time data and normalized Eh vs. time data in the leaching experiments for Horizon C in Core 2E.

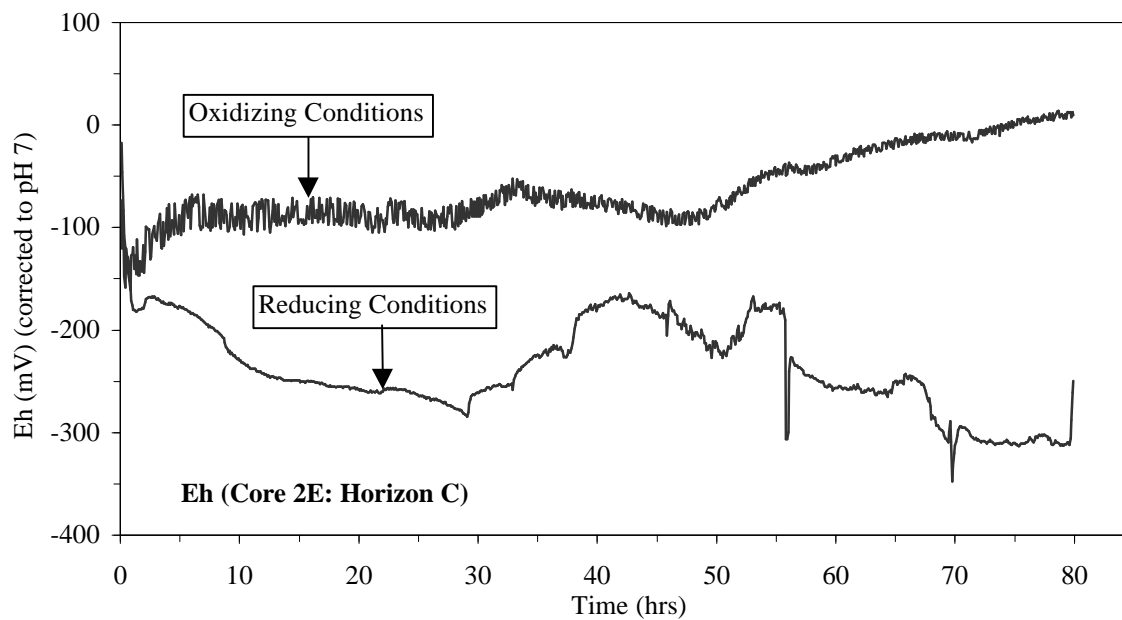


Figure 31. Eh vs. time in the leaching experiments for Horizon C in Core 2E.

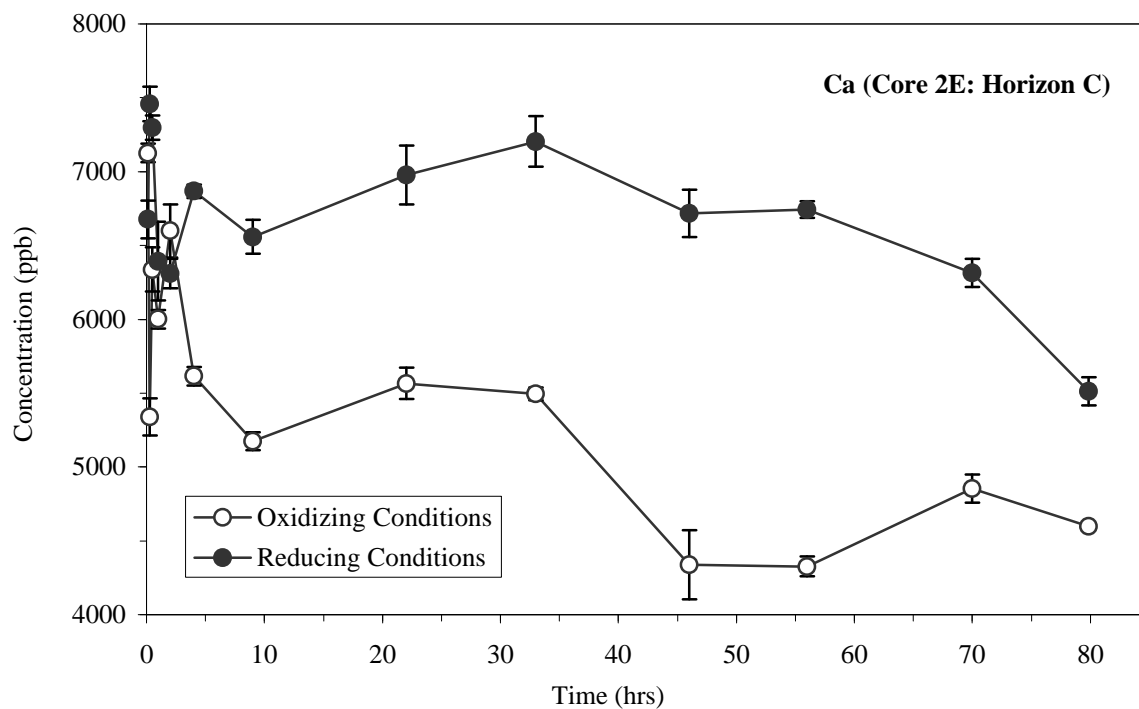


Figure 32. Concentration vs. time for Ca in the leaching experiment of Horizon C in Core 2E.

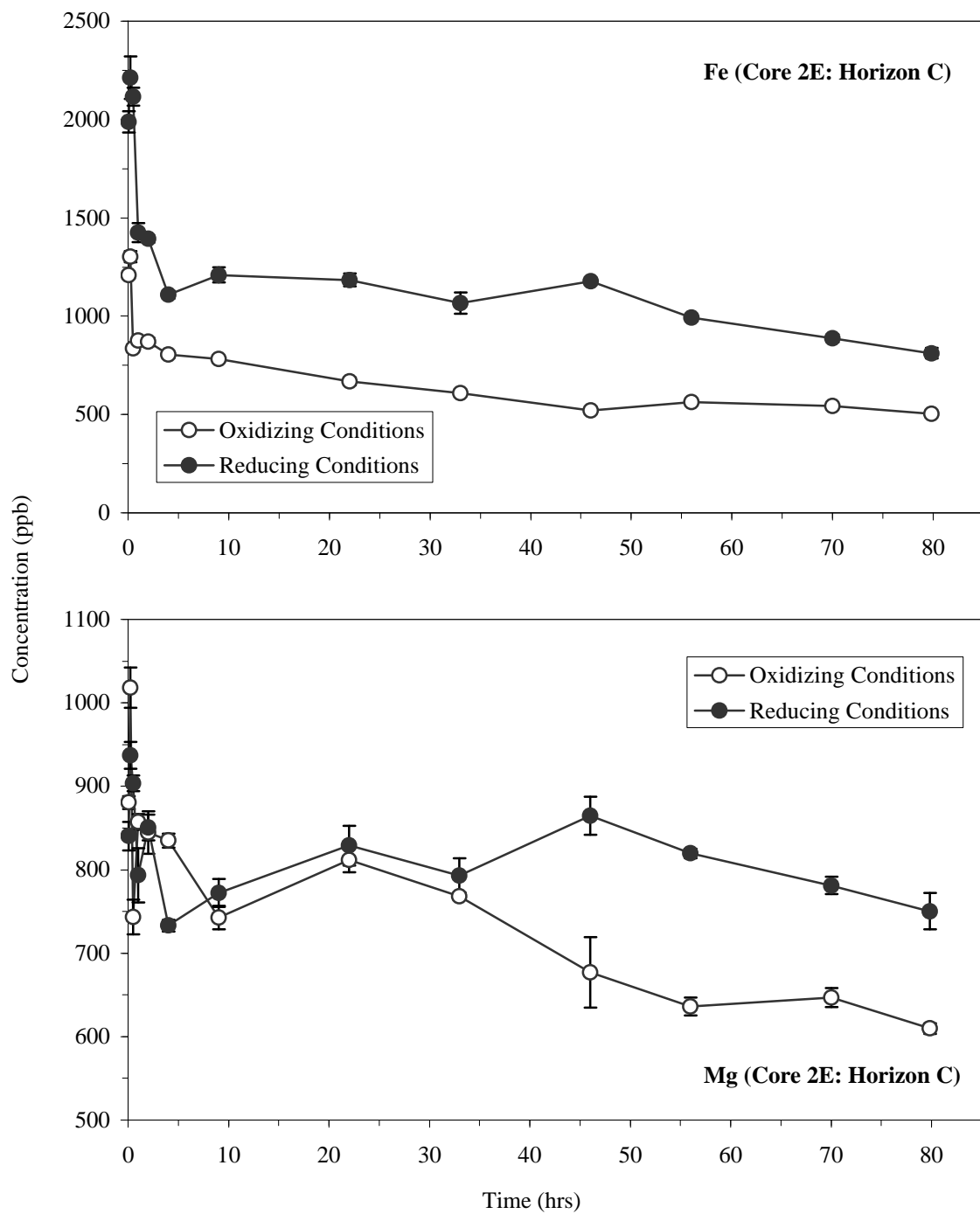


Figure 33. Concentration vs. time for Fe and Mg in the leaching experiment of Horizon C in Core 2E.

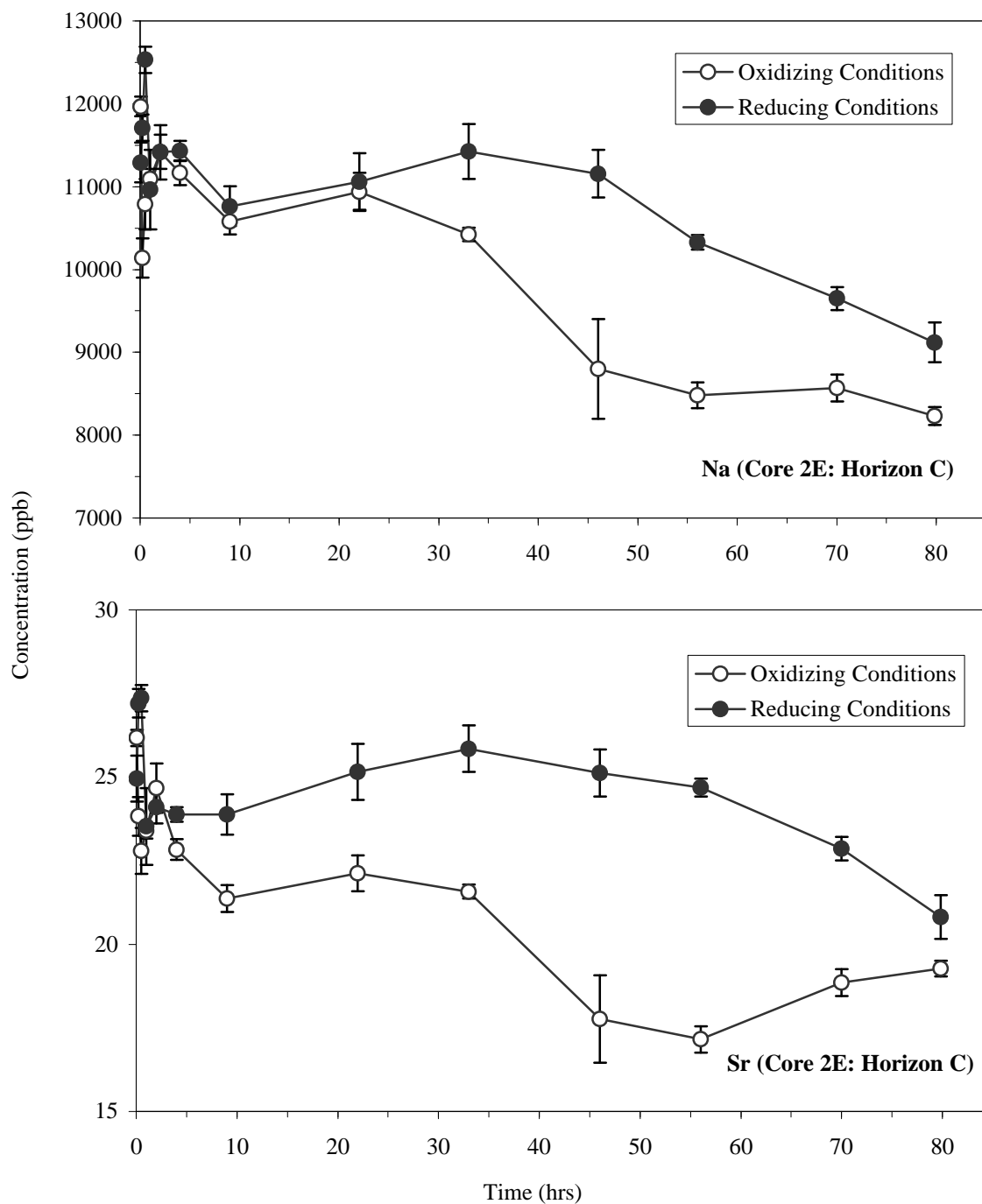


Figure 34. Concentration vs. time for Na and Sr in the leaching experiment of Horizon C in Core 2E.

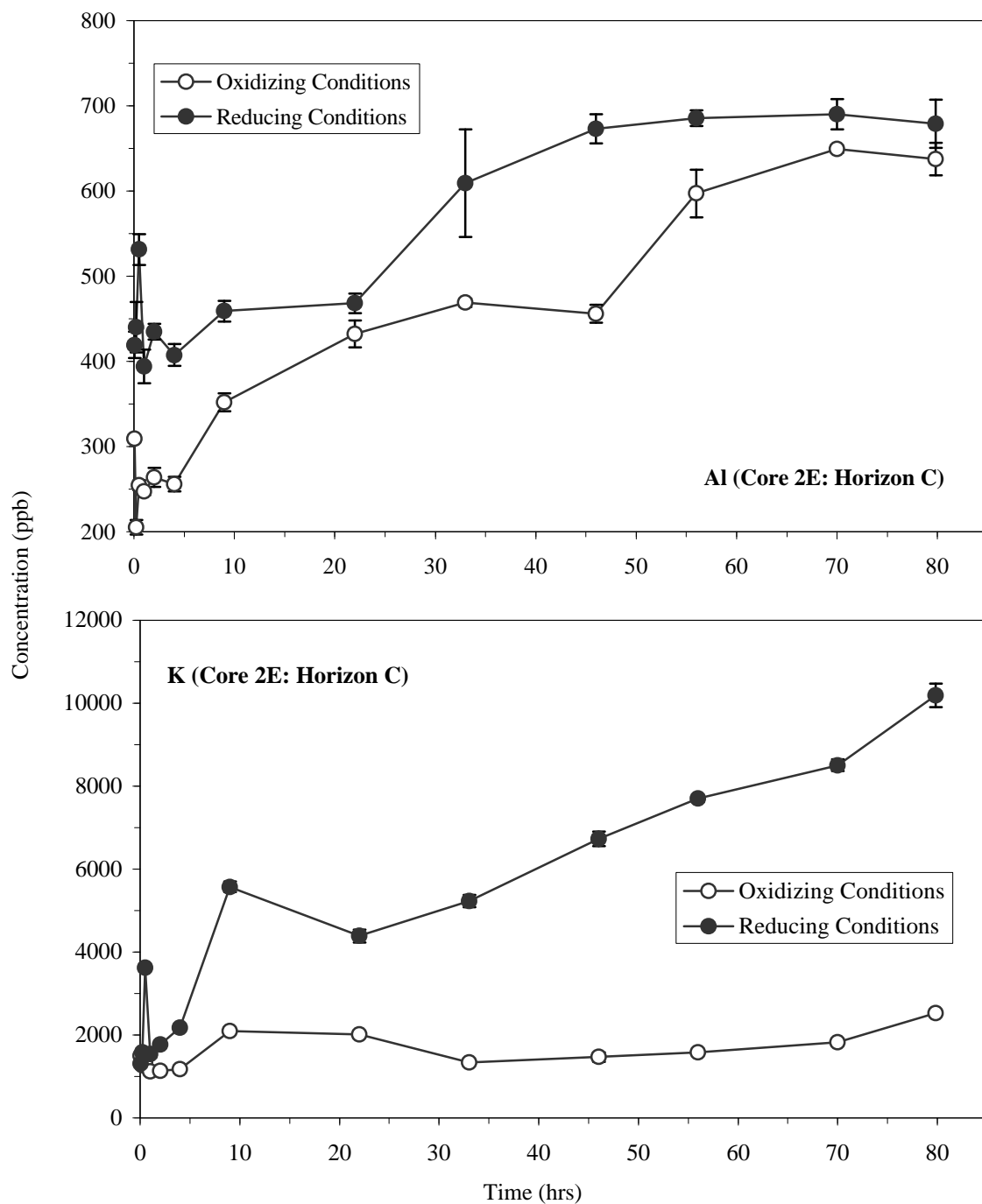


Figure 35. Concentration vs. time for Al and K in the leaching experiment of Horizon C in Core 2E.

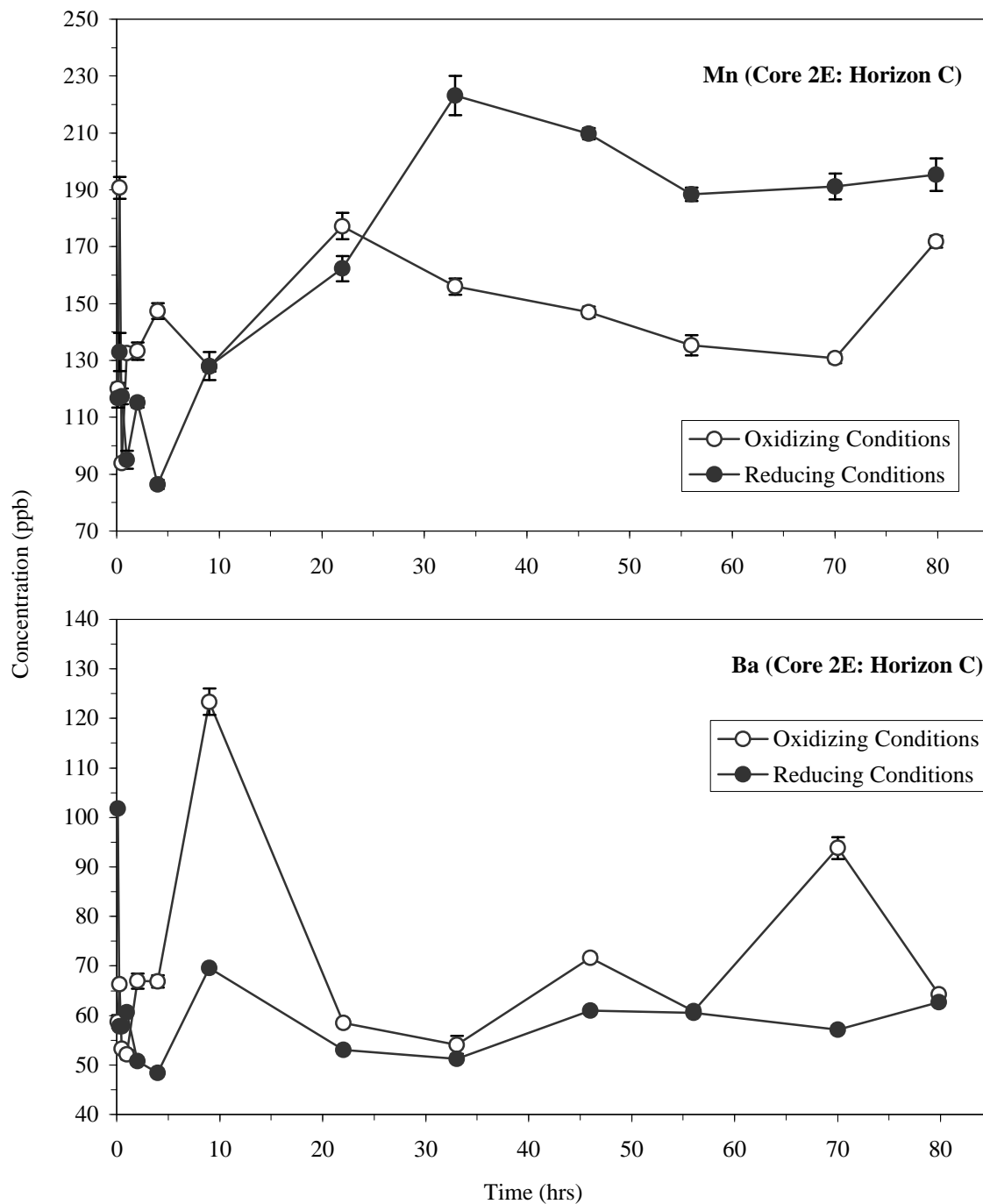


Figure 36. Concentration vs. time for Mn and Ba in the leaching experiment of Horizon C in Core 2E.

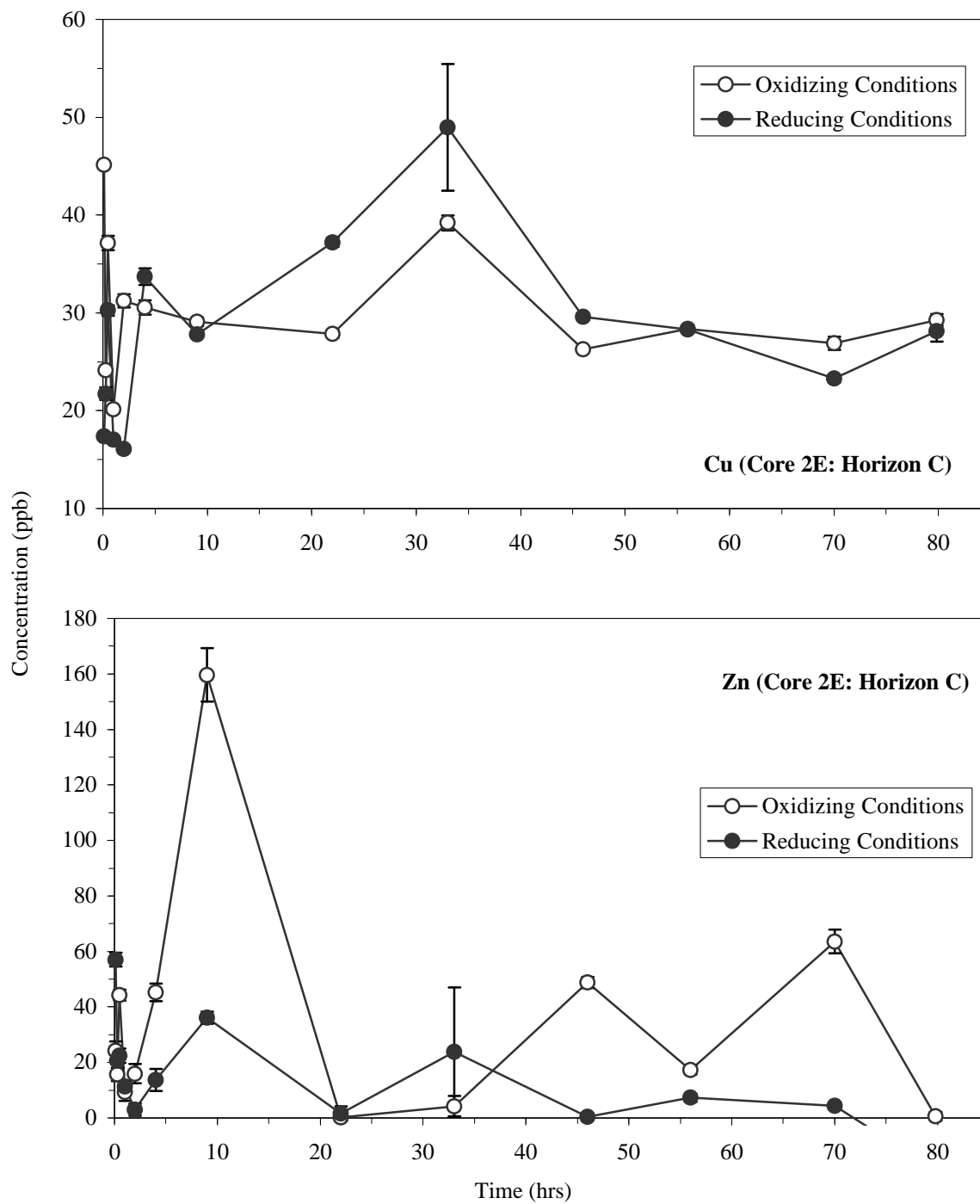


Figure 37. Concentration vs. time for Cu and Zn in the leaching experiment of Horizon C in Core 2E.

CHAPTER 4

DISCUSSION

The fact that most natural systems are not at equilibrium with respect to redox-sensitive species makes redox potential measurements estimates at best. However, the redox potential measurements of the sediment cores in this study, as an evaluation of the in situ redox potential of the sediment, are consistent with redox potential values for waterlogged sediment reported by Patrick et al. (1996). The electrode equilibration times for these measurements were also consistent with those reported by Patrick et al. (1996).

The observed gradual decrease in redox potential following electrode equilibration of the sediment cores is likely a result of the continuing reduction of redox-sensitive species during the decomposition of organic material. A gradual decrease in redox potential following equilibration would probably not be observed if the redox probes were inserted directly in the lake bottom. The interaction of oxygenated groundwater with the saturated sediment has likely resulted in the establishment of steady-state conditions with respect to redox potential. The sealed cores, acting as closed systems, have no source of additional oxygen once it is consumed by decomposition.

The gradual decrease in redox potential following equilibration was not as pronounced in the cores for which redox potential was recorded manually. This may be because equilibration between the electrode and the sediment was hindered due to jostling of the electrodes every time the voltmeter was connected. Utilizing a data logger for these types of redox potential measurements yielded much better results because it allowed the electrodes to remain connected without being disturbed.

At least two factors are likely contributing to the variation in redox potential with depth in the cores obtained from the reservoir. The first is the influence of upwelling oxygenated groundwater. This upwelling is an apparent cause of the general trend of increasing redox potential with depth in the cores collected in May 2001. However, it was not as pronounced in the redox potential of cores collected in August 2001. The difference may be due to the different measurement methods or upwelling may have subsided from May to August as a result of a decrease in local precipitation. August 2001 was significantly drier than May 2001 according to local precipitation data (Figure 38). Piezometer water level measurements were made during the next rainy season (November 2001). The piezometer data confirm the presence of upwelling groundwater but no piezometer measurements were made in August 2001.

The upwelling groundwater could be a result of the construction of the dams themselves. If the streams that were dammed were predominantly gaining with respect to groundwater, the result of damming could be upwelling beneath the created lake (ODNR, 1997). Also, an area like Tallahatchie Co. with relatively low relief, significant precipitation, and permeable soil is a likely candidate for significant groundwater recharge that could result in seasonal groundwater upwelling in settings like Hubbard-Murphree Reservoir. More frequent hydrologic monitoring would resolve this issue.

A second factor influencing redox potential variation in the cores is the influence of organic material. As oxygen is consumed in organic decomposition, redox potential would be expected to drop. It is likely that a horizon with a relatively high organic content would have a lower redox potential.

According to Bennett (2001) the clay content of Hubbard-Murphree sediment has a direct correlation to bulk elemental concentration (Figure 39). Therefore, variations in elemental

concentration with depth in the cores are linked to changes in particle size distribution (i.e. stratigraphy). For example, the decrease in the concentration of Al at a depth of 1.5 meters, in Core 3D, is interpreted to correlate with a change in grain size (from the accumulated sediment to the as-built pre-construction surface) (Figure 40). Based on grain size/concentration comparisons, the pre-construction horizon is interpreted to be at a depth of 1.5 m in Core 3D and 1.2 m in Core 2D.

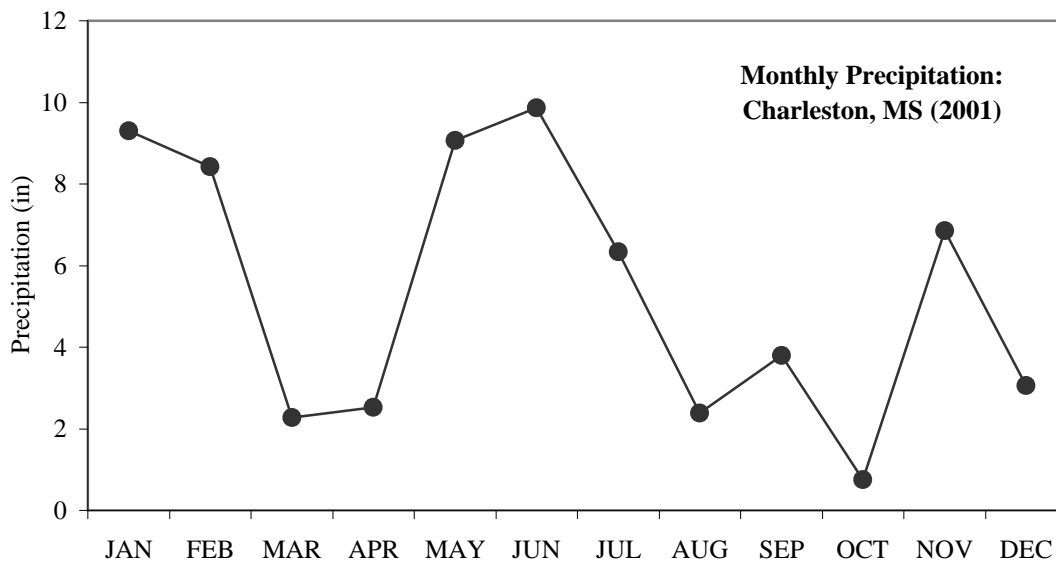


Figure 38. 2001 monthly precipitation data for Charleston, MS (NCDC, 2002).

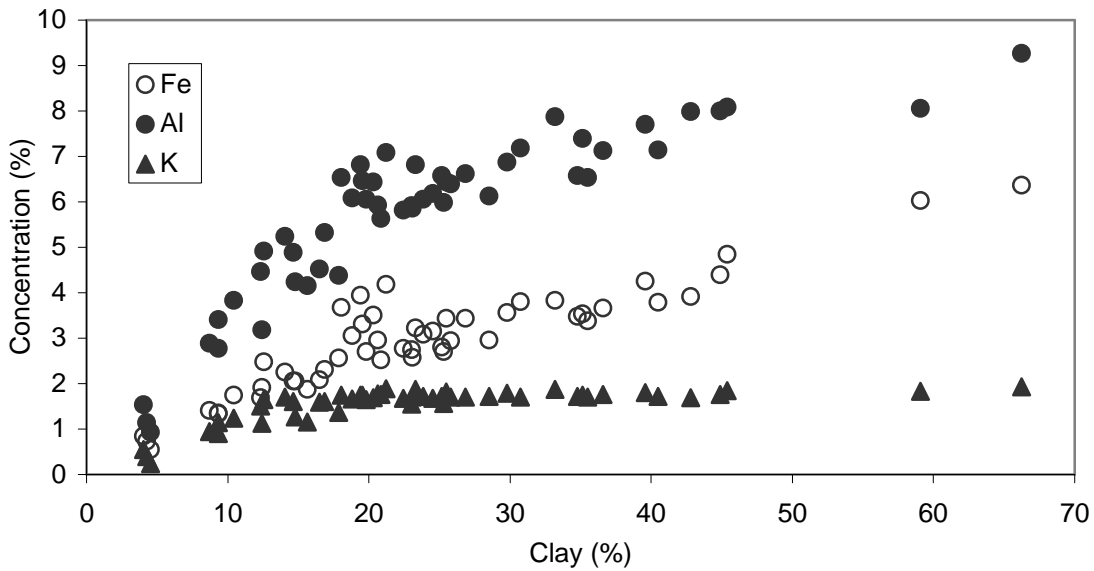


Figure 39. Bulk chemistry as a function of clay % in the Hubbard-Murphree cores collected by Bennett (2001).

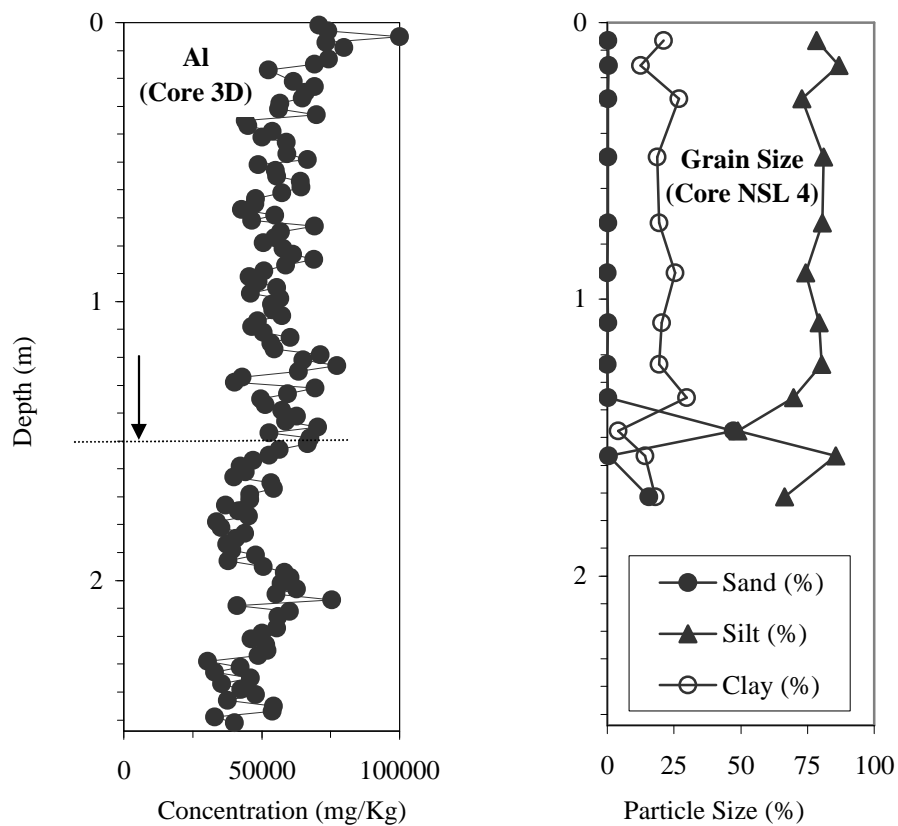


Figure 40. Comparison of variation in bulk chemistry and grain size as a function of depth for select Hubbard-Murphree cores (arrow indicates probable pre-construction surface) (Bennett, 2001).

The results of the leaching experiments in this study indicate that the mobility of all contaminants detected, with the exceptions of Ba, Cu, and Zn, was favored under reducing conditions. This is consistent with results reported by others such as Delaune and Smith (1985). In their leaching study comparing freshwater sediment to saline sediment, freshwater sediment oxidation produced nominal decreases in contaminant mobility. This is in contrast to their saline-sediment leaching results, which indicated that a significant increase in mobility of trace elements was favored by oxidation. The governing factor in their study was reported to be pH. pH variation following saline-sediment oxidation was much more significant (a drop from neutrality to pH 3 following oxidation) than the variation following freshwater sediment oxidation (a drop from neutrality to pH 5.1).

There is a combination of processes that are likely causing mobility to be diminished following oxidation in Hubbard-Murphree sediment. Of the elements in this study that exhibited a general trend of decreased mobility at higher redox potential (Ca, Fe, Mg, Na, Sr, Al, K, and Mn), Fe and Mn are the only two that are redox-sensitive. Their valence and solubility changes as a result of changes in acidity and/or redox potential (Jenne, 1968). Both are more soluble under reducing conditions. An increase in the amount of oxygen in a saturated sediment system will typically result in oxidation of Fe and Mn and precipitation as Fe and Mn oxides. This precipitation is reported to be an important process regulating the availability of trace elements in soils and sediments (Lee, 1973).

According to Lee (1973), freshly precipitated hydrous oxides are thought to be much more effective in scavenging trace elements than are aged materials due to the improved crystallinity and reduced surface area that occurs with time. In the leaching experiments, Fe and Mn oxides that precipitate out of solution are likely incorporating other elements via

coprecipitation and/or adsorption and removing them from solution. Coprecipitation, the “incorporation of a dissolved species as a minor component in a solid phase as that phase itself is precipitated” (Drever, 1997), is likely a significant factor in the immobilization of the elements in this study whose mobility was favored under reducing conditions. In fact, Jeanne (1977) concluded that the most important controls in the distribution of trace elements in soils were adsorption and coprecipitation by solid Fe and Mn oxides and solid organic matter.

In the leaching experiments, the dissolved concentrations of Ca, Fe, Mg, Na, Sr, Al, and Mn were between 15% and 30% greater under reducing conditions than under oxidizing conditions. K exhibited a much greater concentration decrease following oxidation (approximately 75%). K and Na are monovalent cations (i.e. they have one positive charge each). The other detected elements whose mobility was favored under reducing conditions (Ca, Fe, Mg, Sr, and Mn) are all multivalent cations (more than one positive charge each). Therefore, differences in the behavior of K and Na from the multivalent ions would be expected because of the role valence plays in cation exchange. Generally, the higher the valence state of an ion, the stronger the electrostatic forces are governing adsorption and cation exchange (i.e. the exchange of one cation for another on a surface) (Stumm and Morgan, 1970). However, the relative difference in the behavior of K and Na, both monovalent cations, is likely due to a difference in their hydrated radius. By convention, the preferential adsorption sequence known as the lyotropic series governs how close a cation can get to a mineral surface and the order in which ions are preferentially adsorbed. The lyotropic series suggests that the number of charges and the size of the hydrated radius of an ion dictates when that ion will be subject to adsorption in the sequence: $\text{Al}^{3+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$ (Juma, 1998). In this sequence K is favored over Na,

with respect to adsorption. Therefore, as Fe and Mn precipitate out of solution in the leaching experiments, K^+ is more preferentially adsorbed to the precipitate particles than Na^+ .

It is uncertain why Ba, Cu, and Zn were detected in each of the leaching experiments but displayed no significant patterns with respect to concentration as a function of time or redox potential, aside from a few concentration spikes. Zn and Cu are redox-sensitive but were not observably influenced by changes in redox potential. Ba was also not observably affected by changes in redox potential. Overall, the sediments in Hubbard-Murphree Reservoir are relatively lacking with respect to toxic species like As and Cr, which may be present at levels below detection.

pH decreased following oxidation in the leaching experiments. A dominant control on the pH of a system is the activity of H^+ . Therefore, the moderate decrease in pH is likely a result of the release of H^+ as a result of cation exchange or the oxidation of Fe.

CHAPTER 5

SUMMARY

Hubbard-Murphree Reservoir is representative of typical small Mississippi reservoirs in size and construction. Sedimentation in Hubbard-Murphree, based on average sediment thickness and reservoir age, is estimated to be approximately 3.75 cm/yr. Currently there are approximately 1,800 small reservoirs across the nation, including Hubbard-Murphree, in need of rehabilitation due to sedimentation.

According to bulk chemistry analyses, the concentrations of detected elements in the sediment do not vary significantly with depth or spatial distribution. Based on this study and previous studies of Hubbard-Murphree sediment, traditionally toxic trace elements are not present at significant levels. The bulk chemistry of the sediment is controlled primarily by grain size.

The in situ redox potential of the sediment in Hubbard-Murphree Reservoir varies approximately between an Eh of -500 and -300 mV, with some spikes as high as 175 mV at certain depths. Piezometer water level measurements confirm the presence of at least seasonal upwelling groundwater below the lake. This upwelling, along with organic decomposition is likely a factor in the variation of redox potential with depth in the lake sediment.

When lake sediment slurries were exposed to reducing and oxidizing environments in leaching experiments, mobility was favored under reducing conditions for nearly all detected elements. This is attributed to the affect Fe and Mn have when precipitating out of solution. Coprecipitation is likely causing ions that are not redox-sensitive to become attached to freshly precipitated Fe and Mn oxides and removed from solution. For some elements, no concentration change as a result of oxygenation was observed because they were not present at high enough concentrations. Overall, oxygenation resulted in a decrease in concentration of most elements detected. Therefore, because dredging these sediments would likely result in a significant

increase in the oxidation state of the redox-sensitive elements present, immobilization rather than mobilization of the detected trace elements would likely be the result.

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VITA

William Campbell Beard III was born in Selmer, TN on October 15, 1976. He graduated from Pascagoula High School in 1995. He entered Millsaps College in Jackson, Mississippi in the Fall of 1995 and received a Bachelor of Science Degree in Geology in May of 1999. He entered The University of Mississippi in August of 1999 and received a Master of Science degree in Geology in December, 2002.